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ASSESSMENT OF AUTOMOTIVE SULFATE EMISSION CONTROL TECHNOLOGY

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Mobile Source Air Pollution Control
Emission Control Technology Division
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16. ABSTRACT

This contract consists of three parts. Modification I was aimed at developing sorbents for $SO_4^=$ capable of efficiently removing this material from exhaust gas at a low pressure drop over a long service life. Modification II studied three pairs of monolithic automotive oxidation catalysts, nominally identical except for their noble metal components, to determine the effect of composition on the level of $SO_4^=$ emissions. Modification III tested two types of experimental perovskite-based noble metal automotive oxidation catalysts for CO, HC, and SO_2 conversion activity.

In I, a mixture of 85 wt % CaO/10% SiO_2/5% Na_2O was fabricated into 12.7 mm O.D. rings and 4.8 mm pellets. A mixture of 85 wt% $Ca(OH)_2$/15% SiO_2 was prepared as 4.8 mm pellets. These three preparations were tested in canisters mounted in the muffler position of oxidation catalyst-equipped vehicles. All three had high initial efficiency for $SO_4^=$ sorption, but fell off rapidly within 15 000 km of operation to less than 90%.

Modification II showed the following levels of $SO_4^=$ tailpipe emissions when the catalysts were tested on a vehicle over the EPA Sulfate Emission Test using fuel of 320 ppm sulfur: Pt, 30 mg/km; Pt-Pd, 25 mg/km; Pt-Rh, 10 mg/km. In Modification III, a Pt-Perovskite beaded catalyst was compared to a commercial General Motors Pt-Pd oxidation catalyst under normal and elevated temperature operating conditions. In both cases, the commercial catalyst emitted lower levels of CO and HC, as well as $SO_4^=$. A monolithic version of the Pt-Perovskite was also compared to a commercial monolithic catalyst and found to be inferior in CO and HC activity.

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I. Summary

The research described in this report was conducted under an extension of EPA Contract No. 68-03-0497, referred to as Phase II. Results of Phase I of this contract were documented as EPA Report 460/3-76-017(1). Phase I consisted of work in four areas related to sulfate emissions from vehicles:

- Literature search of relevant sources
- Measurement of sulfate emissions from non-catalyst vehicles
- Factors affecting sulfate emissions from oxidation catalyst-equipped cars
- Studies of the feasibility of sulfate traps in vehicle exhaust systems

The current program concentrated on extending the fourth area, sulfate traps. In addition, smaller programs were carried out to investigate the effect of noble metal composition of automotive catalysts on their tendency to convert SO_2 to H_2SO_4, and of the activity of several perovskite-based oxidation catalysts developed by DuPont.

Modification 1 - Sulfate Traps

The trap work was aimed at developing improved sorbents for $SO_4^=$ capable of efficiently removing this material from exhaust gas at a low pressure drop over a long service life. The previous work had shown that good efficiency was possible using small pellets containing primarily $Ca(OH)_2$, with lesser amounts of Na_2O, as the active components. However, pressure drop was unrealistically high. On the other hand, rings of the same composition provided lower pressure drops, but also much reduced sorption efficiency. Accordingly, the focus of the current work was on achieving a satisfactory compromise between sorption and pressure drop.

Two principal paths were pursued; changes in chemical composition, and in geometry. The former approach involved retaining CaO or $Ca(OH)_2$ as the active ingredient, but eliminating sodium. Sodium had been identified as responsible for substantial amounts of SO_2 sorption, in addition to the desired reaction with $SO_4^=$. Sorption of SO_2 is undesirable since it cuts down on the sorbent capacity for $SO_4^=$ and increases the rate of sorbent swelling, which leads to higher pressure drops. The second approach involved the use of smaller rings and larger pellets than had been used previously, in hopes of achieving a better compromise between contact efficiency and pressure drop through the bed.

The removal of Na_2O from the sorbent composition was found to increase the difficulty of compacting sorbent particles with adequate mechanical strength. A number of inert binders, based on Al_2O_3 and/or SiO_2 were mixed with basic calcium compounds, including the hydroxide, oxide and carbonate, in wet and dry preparations. A number of mixing techniques, pelleting conditions, and post-pelleting heat treatments were investigated. In particular, use was made of cement chemistry in preparing experimental sorbents, since the mixtures used were similar to Portland and calcium-aluminate cements.

It was found that a number of very strong pellet samples could be made by these techniques. However, laboratory testing of these pellets showed poor sorption efficiency for $SO_4^=$. It was determined that this was caused by the low porosity of the hard pellets, and also by the absence of sodium. A number of attempts were made to increase porosity, using calcination or burn-out agents. In addition, improved preparation techniques were developed to allow the introduction of controlled quantities of sodium. The goal was to add enough sodium to enhance $SO_4^=$ sorption without greatly increasing sorbent reactivity towards SO_2.

Based on these laboratory studies, two sorbent compositions were identified as sufficiently promising to warrant further vehicle testing. These were a mixture of 85 wt % CaO/10% SiO_2/5% Na_2O, and 85 wt % $Ca(OH)_2$/15% SiO_2. The first sorbent was fabricated into rings of 12.7 mm outside diameter and pellets of 4.8 mm diameter. The rings were smaller than those tested in Phase I of this contract, while the pellets were larger. The second sorbent was made up into the 4.8 mm pellet configuration.

These sorbents were loaded into empty GM catalyst canisters, of 4.2 litre capacity, which were mounted in the muffler position of oxidation catalyst-equipped vehicles. Although $SO_4^=$ sorption efficiency was high initially, it fell off rapidly. None of these sorbents were tested beyond 15 000 km of vehicle operation since sorption efficiency had fallen below 90% in each case by this time.

Modification II - Noble Metal Effect on Catalyst Conversion of SO_2

Three pairs of monolithic oxidation catalysts were prepared by Matthey-Bishop, Inc. The catalysts were made as identical as possible except for their noble metal composition. One pair contained only Pt as the active metal, another pair Pt-Pd, and the third Pt-Rh. The three pairs were tested sequentially on the same vehicle for 12 800 km each and the gaseous and $SO_4^=$ emissions measured. The following table shows the average $SO_4^=$ emissions measured over the EPA Sulfate Emission Test, using a fuel containing 320 ppm sulfur. Emissions of CO and HC were similar for all three sets of catalysts. Both $SO_4^=$ and the regulated emissions did not change measurably over the short duration of these tests.

Catalyst	Average $SO_4^=$, g/km
Pt-Rh	0.010
Pt-Pd	0.025
Pt	0.030

Modification III - Perovskite Catalysts

Two types of experimental catalysts supplied by DuPont were tested for activity for CO and HC removal from exhaust gas and for conversion of SO_2 to $SO_4^=$. Their activity was compared with that of commercial catalysts. These comparisons were made under normal vehicle operating conditions and also under high temperature operation conditions. The latter were obtained by adding port liners and insulation to the test vehicle and resulted in increases in catalyst temperature of 100-200°C.

The first comparison was between a sample of beaded perovskite catalyst, containing Pt at a level roughly comparable to the total Pt-Pd level in commercial GM beaded catalyst, and the GM catalyst. Initially, the activity of these two catalysts was tested sequentially on a conventional vehicle. The GM catalyst, in a 4.2 litre canister, was run for 12 800 km and the Pt-perovskite catalyst for 6 700 km. It was found that CO and HC emissions were substantially lower for the GM catalyst. This was attributed primarily to poor light-off performance of the perovskite catalyst. Surprisingly, $SO_4^=$ emissions from the GM catalyst were also lower.

After vehicle modification to provide higher temperature catalyst operation, emissions tests were repeated on both catalysts. The GM material still retained a substantial advantage, and testing of the beaded samples was concluded.

Samples of a monolithic version of DuPonts's Pt-perovskite catalyst were also tested. In this case, their activity was compared with the commercial Engelhard PTX-IIB monolithic catalyst. Each catalyst was aged for 800 km prior to emissions testing. The test vehicle was kept in the high temperature configuration. The commercial catalyst showed much lower CO and HC emission levels, although it generally resulted in higher $SO_4^=$ emissions. However, the poor CO and HC activity of the perovskite catalyst precluded further work in this program.

II. Introduction

Modification I - Sulfate Traps

The work performed under Phase I of this contract had shown that sulfate traps, consisting of sorbent filled canisters placed in the exhaust system of catalyst-equipped vehicles, could sorb nearly all of the $SO_4^=$ from the exhaust gas. The most efficient and long-lived system had consisted of small (~3 mm) pellets pressed from a powder whose composition was nominally 85 wt % CaO/10% SiO_2/5% Na_2O. However, although this sorbent proved greater than 90% effective for some 40 000 km of operation, pressure drop was a major problem, increasing from an initial value of 1 kPa to a final value of 30 kPa. A typical exhaust catalyst has about 4 kPa pressure drop. The pressure drop increase was ascribed to several factors. As the CaO became sulfated, the pellets tended to swell, since $CaSO_4$ is a larger molecule than CaO. In addition, some powdering was evident, resulting in a filling in of the void volume between pellets.

An attempt to overcome the pressure drop problem through the use of sorbent rings in place of pellets was only partially successful. Rings of about 1.6 cm outside diameter were fabricated from the same material described above. The greater void volume in the bed provided a lower pressure drop initially, 0.5 kPa, and an increase to only 4 kPa after 20 000 km of testing. However, the poorer gas-solid contacting produced a much lower $SO_4^=$ removal efficiency, 80% initially, but falling off rapidly after only about 5 000 km.

Based on this experience with pellets and rings made up of the CaO/SiO_2/Na_2O composition, several further approaches to achieving a better trade-off between pressure drop and sorption efficiency suggested themselves:

- Change in chemical composition

The vehicle tests had shown that substantial quantities of SO_2 were being picked up as well as $SO_4^=$. Preferably, only $SO_4^=$ should be sorbed, since SO_2 is a normal and relatively innocuous component of exhaust gas in all motor vehicles (catalyst and non-catalyst) and its sorption lowers capacity for $SO_4^=$ pick-up. Laboratory studies had shown that the sodium was primarily responsible for SO_2 sorption. Therefore, it was postulated that its removal would result in pellets with greatly increased capacity for $SO_4^=$. Furthermore, their sulfation rate, hence swelling and resultant pressure drop increase, should be minimized. Thus, a major part of Phase II of this contract has been concerned with the formulation and fabrication of sodium-free, calcium-based sorbent preparations.

- Change in sorbent geometry

Phase I had shown that 3 mm pellets were too small to allow low pressure drop and 1.6 cm O.D. rings too large for good gas-solid contacting. Therefore, it was decided to try larger pellets and smaller rings, maintaining the original sodium-containing formulation, in an effort to achieve a better balance between pressure drop and sorption efficiency.

Modification II - Noble Metal Effect on Catalyst Conversion of SO_2

Other work has indicated that catalyst type can influence the extent of SO_2 conversion to $SO_4^=$ in exhaust gas(2,3,4). These studies showed that a Pt-Rh containing catalyst tended to produce less $SO_4^=$ than Pt or Pt-Pd catalysts. However, these studies were confounded by other properties in which these catalysts differed beyond just noble metal composition. They were manufactured by different companies and were dissimilar in washcoat properties and method of metal impregnation. In an effort to separate out the effect of noble metal composition from other factors, it was decided to request a single manufacturer, in this case Matthey-Bishop, Inc., to prepare three pairs of monolithic catalysts. These were to be as identical as possible in all respects, save their noble metal composition. By then testing the three pairs on the same vehicle under similar operating conditions, it should be possible to determine if noble metal composition plays a role in oxidation catalyst selectivity for SO_2 conversion. If no differences were observed, it would have to be concluded that the reported effects in the literature were due to other factors. If a significant difference were obtained, then it could be concluded that noble metal composition does play a role, although further work would still be necessary to determine if it were the sole or even the dominant effect.

Modification III - Perovskite Catalysts

DuPont has been working towards the development of lead-tolerant automotive oxidation catalysts. Their approach has been to use noble metal supports capable of anchoring the metals tightly enough to prevent the high temperature sintering normally seen with conventional alumina supports. By means of this technique, they hope that catalysts can be operated at temperatures sufficiently high to prevent lead deposition and reaction with the catalyst, while avoiding thermal degradation. Such temperatures have been reported by DuPont to be in the vicinity of 730°C(5). At the time Modification III was begun, there appeared no practical means of consistently achieving such temperatures without vehicle modifications which would lower fuel efficiency. In view of the growing importance of good fuel economy, it was agreed that the DuPont catalyst would be tested in this program only with unleaded gasoline. Catalyst temperatures would be raised above usual levels, but only through techniques such as port liners and insulation, which should not affect fuel economy.

III. Modification I - Feasibility Studies of Sulfate Removal From Exhaust Gas By Traps

III.1 Summary of Results

Initially a number of laboratory preparations were made of sodium-free compositions containing basic calcium compounds and inert binders. These preparations used both wet and dry mixing techniques. It was found difficult to fabricate strong pellets from dry mixtures, but wet methods, relying on cement chemistry, resulted in very strong pellets. Laboratory activity screening showed poor sorption efficiency, however, due in part to poor porosity of the very hard pellets. It was also found that the presence of some sodium greatly enhanced sorption efficiency.

Attention was, therefore, directed to methods for improving pellet porosity, through the use of calcination and of burn-out agents, and of controlled sodium addition. Improved porosity was achieved through the burning out of cellulose and starch, with some improvement in sorption efficiency. A greater improvement was achieved by the development of better washing techniques, which allowed controlled addition of sodium to the sorbent preparations in amounts which enhanced sorption efficiency towards $SO_4^=$, without greatly increasing sorption of SO_2.

Two preparations were chosen for vehicle testing; 85 wt % CaO/10% SiO_2/5% Na_2O, and 85% CaO/15% SiO_2. The former was fabricated into rings of 12.7 mm outside diameter and 4.8 mm pellets. The latter was made up as 4.8 mm pellets only. In no case was satisfactory $SO_4^=$ sorption achieved during the vehicle runs, and no sorbent was tested for more than 15 000 km.

III.2 Introduction

In the Final Report of Phase I of this contract$^{(1)}$, laboratory preparation and vehicle testing of pellets and rings prepared from "benchmark" material, nominally a ratio of 85/10/5 of $Ca(OH)_2/SiO_2/Na_2O$, was described. Although the benchmark pellets exhibited excellent activity for $SO_4^=$ removal in laboratory reactor and vehicle trap tests, one major problem appeared. The pressure drop through the vehicle trap increased over the course of the test from an initial value of 1 kPa (~4 inches H_2O) to some 30 kPa. This was attributed to several factors: swelling of the pellets as sulfation proceeded, since $CaSO_4$ is a larger molecule than is $Ca(OH)_2$; and collection of fine particles, attritted from the pellets, in the relatively densely packed bed.

A variety of approaches suggested themselves as possible solutions to the pressure drop problem:

A. Use a trap bed with greater void volume

B. Prepare harder sorbent particles to reduce level of fines in the bed

C. Reduce the SO_2 sorption ability of the sorbent, thereby reducing sulfation rate and hence degree of swelling. This would also provide the added benefit of increased sorption capacity for $SO_4^=$.

As a first step in attempting to improve trap performance, sorbent particles in the form of rings were prepared from the benchmark composition. Vehicle testing of these rings, also reported in Reference 1 showed greatly improved pressure drop, but also considerable reduction in $SO_4^=$ sorption performance. Thus, the greater void volume afforded by rings compared to pellets did reduce pressure drop, as predicted, but the resulting decrease in gas-solid contacting efficiency was apparently too great.

As a result of the above work done under Phase I of the contract, it was concluded that Phase II should try the following approaches.

A. Retain the benchmark composition because of its known ability to remove $SO_4^=$ from exhaust gas, but attempt to optimize particle geometry to obtain a satisfactory compromise between pressure drop and contacting efficiency. This resulted in the preparation of smaller rings and larger pellets than those reported under Phase I.

B. Remove Na from the sorbent composition, since some preliminary laboratory results obtained in Phase I indicated that much of the SO_2 sorption effect was due to its presence. This work in Phase I also suggested that the removal of Na adversely affected the strength of sorbent particles. Therefore, a variety of binding agents, compounding techniques, and heat treatments would have to be studied in efforts to obtain sorbent particles of the requisite hardness, which retained sufficient porosity for good $SO_4^=$ sorption activity.

Based on these considerations, a large number of Ca-based sorbents have been prepared, with a number of binders, in physical and chemical combinations. Both dry and wet mixing techniques have been employed, as have a variety of pre- and post-pelleting treatments. Those preparations capable of compaction into strong pellets have been tested in a laboratory reactor for $SO_4^=$ sorption activity. In addition, attempts have been made to correlate physical properties of these pellets, such as surface area, pore volume, and pore size distribution, with sorption activity. Finally, vehicle tests of full size traps have been conducted using rings and pellets made from benchmark material. The rings were smaller and the pellets larger than their counterparts from Phase I. In addition, pellets made from a Na-free composition have also been vehicle tested.

III.3 Sorbent Composition and Pilling

The aim of these studies was to determine the suitability of basic inorganic compounds of calcium, combined physically or chemically with inorganic binders, for fabrication into compacted shapes, and the efficiency of such particles for $SO_4^=$ removal.

These preparations differed from the benchmark sorbent, which is of nominal composition 85 CaO/10 SiO_2/5 Na_2O, in containing little or no sodium. The sodium component has previously been shown to be responsible for sorption of SO_2 which is undesirable from the standpoint of loss of trap capacity for $SO_4^=$ and too rapid swelling.

III.3.1 Dry Mixtures

III.3.1.1 Physical Combinations - Pelleting

A series of nine dry mixtures were prepared using calcium oxide, calcium hydroxide, and calcium carbonate, each with three binder systems. Selection of suitable ingredients for these mixtures followed a survey of commercially available materials. For the dry mixtures, a requirement for the ingredients is that they flow readily in the pelletizing operation. In the automatic pellet press, the dry material must flow without caking or binding to fill 3 mm dies. From our experience, materials which are granulated in the range of 14-35 mesh have suitable flow properties.

For silica and alumina binders, chemical reactivity is important in addition to flow properties. Forms of silica and alumina which are "hydrated", rather than calcined, are believed to be the best choice, providing chemical reactivity and good binding.

Alcoa Hydrated Alumina C-31 (coarse) (64.9 wt % equivalent Al_2O_3) was selected as a reactive form of alumina with good flow properties. Similarly, PPG Hi-Sil 210 hydrated amorphous silica (94 wt % equivalent SiO_2) was chosen as a suitable source of silica. A description of the materials selected for the dry mixtures is given in Appendix A.

These combinations of calcium compounds with silica and/or alumina were then evaluated in pelleting trials using a sixteen-station rotary tablet press having 3.2 mm dies and upper and lower punches. The results of these trials are given in Appendix Table B-1.

All formulations flowed well during pelleting. However, those mixtures containing calcium oxide or calcium carbonate presented severe problems during attempts to make hard pellets. The machine was operated beyond recommended limits in tests with these mixtures. Even with the use of 3% Sterotex (as die lubricant), reasonable pellets were obtained only with mixture No. 5 (85% CaO/15% Al_2O_3). However, these pellets disintegrated after heating at 95°C.

For the mixtures containing calcium hydroxide, no problems were encountered during pelleting. Hard pellets were obtained with each of the three binder systems after heat treating at 315°C. The pellets made from calcium hydroxide in combination with alumina, or with silica/alumina, were slightly harder than those made with silica.

This lack of success in dry-compacting calcium oxide and calcium carbonate was probably due to the hardness of these materials and difficulty in obtaining cohesion between grain particles. An attempt was made to wet-granulate finely powdered calcium carbonate, with only fair success. The resulting material flowed poorly during pelleting and, even by hand-filling the dies, no coherent pellets could be made. This is in contrast with wet granulation of finely powdered calcium hydroxide. This material flowed well during pelleting and very hard pellets were made from 100% calcium hydroxide, as shown in Table III-1.

TABLE III-1

EFFECT OF HEAT TREATMENT ON CRUSH STRENGTH

Heat Treatment	Crush Strength of 100% $Ca(OH)_2$ Pellets (kg)
initial	7.7
48 h @ 95°C + 6 h @ 150°C	7.6
16 h @ 315°C	8.6

No further dry mix pelleting studies were performed with calcium oxide or calcium carbonate. All the calcium hydroxide preparations, including the pellets from 100% calcium hydroxide were evaluated for $SO_4^{=}$ sorption efficiency using the laboratory reactor, as discussed in Section III.3.3.

III.3.1.2 Chemical Combinations - Pelleting

Table III-2 lists results using dry mixtures of calcium hydroxide with silica and/or alumina to give the stoichiometric proportions: $(CaO)_3\ SiO_2$, $(CaO)_3\ Al_2O_3$, and $(CaO)_3\ (SiO_2\ Al_2O_3)_{1/2}$. For these mixtures, the binder concentrations are higher than the 15% employed above. For $(CaO)_3\ SiO_2$, 21.3% silica is used, and for $(CaO)_3\ Al_2O_3$, 31.4% alumina is required. The mixture corresponding to $(CaO)_3\ (SiO_2\ Al_2O_3)_{1/2}$ contains 9.9% silica and 16.8% alumina.

The crush strength of the unfired pellets from each of these mixtures was lower than that of the corresponding preparation using less binder. For example, 85 $Ca(OH)_2$/15 SiO_2 sorbent had a crush strength of 4.1 kg, whereas $(CaO)_3\ SiO_2$ sorbent had a crush strength of only 3.4 kg. The hardest pellets were obtained using the $(CaO)_3\ Al_2O_3$ composition (3.8 kg). Even these were weaker than the corresponding pellets from 15% alumina (4.5 kg).

These pellets were then fired for two hours at 1350°C, which is representative of commercial conditions for making calcium silicates and calcium aluminates, as in cement manufacture. The results are given in Table III-3. As a result of this heat treatment, the pellets corresponding to $(CaO)_3\ SiO_2$ and $(CaO)_3\ (SiO_2\ Al_2O_3)_{1/2}$ crumbled to powder. The pellets of $(CaO)_3\ Al_2O_3$ remained intact; however, crush strength decreased from 3.8 kg to 2.9 kg. Therefore, this approach to sorbent fabrication was not pursued further. With sufficient effort, conditions might be found where CaO and Al_2O_3 or SiO_2 particles could be effectively sintered to give strong pellets; however, because the sorbent would be in the form of CaO, rehydration or carbonation under vehicle exhaust conditions holds the likelihood of breaking up the sintered structure.

III.3.2 Wet Mixtures

III.3.2.1 Chemical Combinations by Co-Precipitation

The three chemical combinations discussed in Section III.3.1.2 were also prepared by a co-precipitation technique. Appendix Table B-2 describes the materials and procedure used, while Table III-4 gives the chemical and physical properties of the pellets obtained from the three preparations. Very hard pellets were obtained from the $(CaO)_3\ SiO_2$ preparation (9.4 kg). For the $(CaO)_3\ Al_2O_3$ preparation, the pellets cracked and became weak after treatment at 315°C (crush strength 1.6 kg) even though the initial appearance and hardness was satisfactory (crush strength 4.4 kg). Hard pellets were obtained from the $(CaO)_3\ (SiO_2\ Al_2O_3)_{1/2}$ combination (initial crush strength 7.2 kg, although these became somewhat weaker after 315°C (5.0 kg).

TABLE III-2

CHEMICAL COMBINATIONS FROM DRY MIXES; PELLETING TRIALS

Nominal Composition:	$(CaO)_3SiO_2$	$(CaO)_3Al_2O_3$	$(CaO)_3(SiO_2Al_2O_3)_{1/2}$
Ingredients, Wt. % (1)			
Calcium Hydroxide (2)	78.7	68.6	73.3
Silica (3)	21.3	--	9.9
Alumina (4)	--	31.4	16.8
Operation During Pelleting			
Flow into Dies:	good	good	good
Ease of Compaction/ Ejection:	fair	good	good
Crush Strength of 3.2 mm Pellets			
Initial Crush Strength (kg)	1.9	3.4	7.6
Crush Strength after 16 h @ 515°C (kg)	2.4	3.8	3.5
Notebook Reference 4349	50-1	50-2	50-3

(1) Percentages given are for pure ingredients, i.e., $Ca(OH)_2$, SiO_2, and Al_2O_3. In the actual formulations, the percentages are adjusted to allow for water content of the ingredients.

(2) Granulated calcium hydroxide, 85 wt. % $Ca(OH)_2$, balance water.

(3) Hi-Sil 210 Hydrated Amorphous Silica, 94 wt. % SiO_2, balance water.

(4) Alcoa Hydrated Alumina C-31 (coarse), 64.9 wt. % Al_2O_3, balance water.

TABLE III-3

EFFECT OF SINTERING AT 1350°C PELLETS PREPARED FROM DRY MIXES

Nominal Composition:	(CaO)$_3$ SiO$_2$	(CaO)$_3$ Al$_2$O$_3$	(CaO)$_3$ (SiO$_2$ Al$_2$O$_3$)$_{1/2}$
Ingredients, Wt. %			
Calcium Hydroxide	78.7	68.6	73.3
Silica	21.3	—	9.9
Alumina (1)	—	31.4	16.8
Crush Strength of 3.2 mm Pellets (kg)			
Initial	1.9	3.4	3.6
After 16 hrs. @ 315°C	2.4	3.8	3.5
After 2 hrs. @1350°C	powdered	2.9	powdered
Notebook Reference 4340	59-1, 116	59-2, 116	57-3, 116

(1) Alumina as hydrated alumina, 64.1 wt. % Al$_2$O$_3$, balance water.

TABLE III-4

CHEMICAL COMBINATIONS BY COPRECIPITATION; PELLETING TRIALS

Nominal Composition:	$(CaO)_3\ SiO_2$		$(CaO)_3\ Al_2O_3$		$(CaO)_3(SiO_2Al_2O_3)_{1/2}$	
Sterotex	3%		3%		3%	
Analysis (1)	Calculated	Found	Calculated	Found	Calculated	Found
CaO	73.7	72.2	62.2	44.4	67.5	58.2
SiO_2	26.3	23.5	--	--	12.0	9.8
Al_2O_3	--	--	37.8	32.5	20.5	18.1
Na_2O	--	3.5	--	7.0	--	14.6
Operation During Pelleting						
Flow into Dies:	good		excellent		good	
Ease of Compaction/ Ejection:	good		good		good	
Crush Strength of 3.2-mm Pellets						
Initial Crush Strength (kg)	6.3		4.4		7.2	
Crush Strength after 16 h @ 315°C (kg)	9.4		1.4 (2)		5.0	
Notebook Reference 4349 -	28		30		41	

(1) Analysis for elements is by emission spectroscopy on material which has been calcined for 5 h at 815°C.

(2) Cracks formed in pellets

Chemical analyses on these preparations after calcining at 815°C are given in Table III-4. These analyses indicated that the water-wash procedure used for these preparations was not satisfactory in removing excess sodium. Expressing sodium content as Na_2O, these materials contained the equivalent of 3.5-14.6 wt % Na_2O. One of our goals was to produce sodium-free sorbents which would be unreactive to SO_2. Therefore, three new preparations of $(CaO)_3\ Al_2O_3$, $(CaO)_3\ SiO_2$ and $(CaO)_3\ (SiO_2\ Al_2O_3)_{1/2}$ were made with more thorough water-washing. The new wash procedure consisted of reslurrying the filter cake with distilled water in a separate vessel, stirring 30 minutes, and refiltering. This sequence was repeated three times. Satisfactory low sodium values were obtained using the revised procedure. Analyses of these preparations and the results of crush strength tests on the pelleted materials are given in Table III-5. Residual sodium contents were very low (0.5-2.3% expressed as Na_2O) relative to levels obtained previously (3.5-14.6%). Low sodium content is desirable because such sorbents may be expected to be more selective in sorbing $SO_4^=$ rather than SO_2. However, an unexpected result of the new procedure and lower sodium levels was a reversal in crush strengths. Previously, $(CaO)_3\ SiO_2$ pellets were the strongest and $(CaO)_3\ Al_2O_3$ pellets were the weakest. With the new procedure, the $(CaO)_3\ Al_2O_3$ pellets were the strongest, having a crush strength of 10.5 kg, whereas a crush strength of only 1.4 kg was obtained previously. Pellets from $(CaO)_3\ SiO_2$ had a crush strength of 3.6 kg by the new procedure, whereas a strength of 9.4 kg was obtained previously. No significant change in crush strength occurred in preparations of the mixed sorbent, $(CaO)_3\ (SiO_2\ Al_2O_3)_{1/2}$ (crush strengths 5.0 and 4.8 kg).

Of the six preparations by coprecipitation, we selected $(CaO)_3\ Al_2O_3$, made by the improved water-wash procedure, as the best candidate for further evaluations. Pellets of this material were tested for $SO_4^=$ trapping efficiency in a laboratory reactor, as described in Section III.3.3.

III.3.2.2 Application of Cement Chemistry to Sorbent Preparation

Surprisingly, the addition of SiO_2 or Al_2O_3 to $Ca(OH)_2$ was found, in dry mixes, to lower the crush strength of compacted pellets rather than to provide binding action, as discussed in Sections III.3.1.1 and III.3.1.2 and shown below. However, as reported in Section III.3.1.1, strong pellets could be made from $Ca(OH)_2$ with no binder by a wet granulation technique. Therefore, it was decided to look at this method in more detail, along with the use of binders. A number of preparations

	Calcium Hydroxide + Binder				
Binder:	None	15% SiO_2	21.3% SiO_2	15% Al_2O_3	31.4% Al_2O_3
Crush Strength (kg)	8.6	4.1	2.4	4.5	3.0

TABLE III-5

[illegible]

Improved Water Wash Procedure

Nominal Composition	CaO, SiO$_2$			CaO, Al$_2$O$_3$			CaO, SiO$_2$, Al$_2$O$_3$		
	Calculated	First Preparation[1]	Second Preparation[2]	Calculated	First Preparation[1]	Second Preparation[2]	Calculated	First Preparation[1]	Second Preparation[2]
Analyses[3]									
CaO	73.7	72.2	74.5	62.2	64.6	66.6	67.5	58.2	66.6
SiO$_2$	26.3	23.5	24.0	—	—	—	12.0	9.8	12.5
Al$_2$O$_3$	—	—	—	37.8	32.5	30.2	20.5	18.1	20.0
MgO	—	3.5	2.3	—	7.0	1.1	—	14.6	0.5
Crush Strength of 3.2-mm Pellets									
Initial Crush Strength, kg	—	6.5	2.1	—	4.6	6.2	—	7.2	6.1
Crush Strength after 20 hours @ 325 °C, kg	—	9.6	1.6	—	2.6	10.5	—	5.8	4.8
[illegible]	—	28	90	—	37	62	—	62	84

(1) Using original water wash procedure.
(2) Using improved water wash procedure. (The filter cake is reslurried three times with distilled water and refiltered.)
(3) Analysis on samples heated 2 hours at 825°C.

were made using wet pastes of the mixtures, which were then dried and granulated prior to pelleting. In this approach, we were guided by the chemistry of calcium-derived cements. These are "hydraulic" cements, hardening by the addition of water due to formation of hydrated phases of calcium silicates and calcium aluminates. It was hoped to use hydraulic cements to "cement together" particles of calcium hydroxide or calcium carbonate to give a mechanically strong, although porous, structure.

Hydraulic cements were incorporated into sorbent compositions by either (1) combining ingredients which react with each other and with water to harden, or (2) using commercially available hydraulic cements which can bind calcium hydroxide or calcium carbonate particles analogous to the way that aggregate stone is bound in making concrete. The first approach is illustrated by "pozzolanic cements", described in Section III.3.2.2.1. The latter by Portland and calcium aluminate cements, as described in Section III.3.2.2.2.

III.3.2.2.1 Wet Mixtures of Calcium Hydroxide With Silica and Alumina - A Type of Pozzolanic Cement

The pozzolanic cements are mixtures of hydrated lime (calcium hydroxide) with various sources of active aluminum silicates, known as pozzolanas. In the presence of water, the pozzolana reacts with calcium hydroxide to form hydrated calcium aluminates and silicates, which constitute the binding matrix. We were seeking to agglomerate powdered calcium hydroxide by such a mechanism.

A series of mixtures of calcium hydroxide with various sources of silica and alumina, which are described in Tables III-6 and III-7, were prepared. Calcium hydroxide was mixed with sufficient binder to give 5 or 15 wt % alumina and silica. The mixture was blended with water to form a paste, and allowed to age 24 hours in a covered vessel. The resulting material was dried at 65°C and granulated to 14-40 mesh before pressing to 3.2 mm pellets.

Table III-6 lists the results of pelleting trials with combinations of calcium hydroxide and various sources of silica. These consist of a hydrated amorphous silica, an anhydrous amorphous silica, diatomites - both calcined and uncalcined, and a colloidal silica. The hardest pellets of all, after heat treating at 315°C, were obtained with 15 wt % uncalcined diatomite. These have a crush strength of 12.8 kg, which is significantly harder than corresponding pellets obtained from 100% calcium hydroxide (8.6 kg). Crush strength using 5% of uncalcined diatomite is only slightly lower (11.0 kg). The softest pellets were obtained from calcined diatomite, having a crush

TABLE III-6

[illegible]

Composition (1)	Crush Strength of 1/8 in Pellets, lb: Initial	Crush Strength of 1/8 in Pellets, lb: After Heat Treating (2)	Laboratory Reactor Test: Total Exposure to Test, Hours	SO2 Trapping Efficiency, %	H2S Trapping Efficiency, %	Final Crush Strength of Pellets, lb	Notebook Reference (NB)
Benchmark Sorbent: [illegible]	6.6	6.3	1.3 2.6 6.9	96 96 72	85 48 33	6.6	46
85 Wt. % Calcium Hydroxide 15 Wt. % Hydrated Amorphous Silica (Hi-Sil 233)	5.8	7.4					67-1
95 Wt. % Calcium Hydroxide 5 Wt. % Hydrated Amorphous Silica (Hi-Sil 233)	10.6	9.5					67-2
85 Wt. % Calcium Hydroxide 15 Wt. % Diatomite (uncalcined) (Dicalite [illegible])	7.6	12.8	1.3 2.7 5.7	97 71 62	38 18 12	11.5	68-1
95 Wt. % Calcium Hydroxide 5 Wt. % Diatomite (uncalcined) (Dicalite [illegible])	4.5	12.0					68-2
85 Wt. % Calcium Hydroxide 15 Wt. % Diatomite (calcined)	2.3	3.2					67-3
85 Wt. % Calcium Hydroxide 15 Wt. % Anhydrous Amorphous Silica (Syloid 244)	7.8	9.6					68-3
85 Wt. % Calcium Hydroxide 15 Wt. % Colloidal Silica ([illegible])	2.6	4.8					71

(1) For pelleting, all mixtures are blended with 2.0 wt. % [illegible] lubricant.

(2) [illegible]

TABLE III-7

[illegible]

Composition (1)	Crush Strength of 3.2 mm Pellets, kg Initial	After Wet Treating (2)	Laboratory Reactor Test: [illegible] v/v/hr., [illegible] Total Exposure To Test, Hours	[illegible] Trapping Efficiency, %	[illegible] Trapping Efficiency, %	Final Crush Strength of Pellets, kg	Notebook Reference [illegible]
							69-4
78.4 Wt. % Calcium Hydroxide 21.6 Wt. % Hydrated Alumina (Alcoa C-33)(3)	6.4	9.6	1.2 3.5 6.0	60 51 38	0 – 0	12.7	
							69-5
92.8 Wt. % Calcium Hydroxide 7.2 Wt. % Hydrated Alumina (Alcoa C-33)	8.1	12.7	1.3 4.0 6.0	75 57 34	23 15 20	11.5	
							69-7
83 Wt. % Calcium Hydroxide 17 Wt. % Kaolinite (uncalcined) ([illegible])(4)	4..	12.4					
							69-8
85 Wt. % Calcium Hydroxide 15 Wt. % Kaolinite (calcined) ([illegible])(5)	5.2	9.6					
							69-6
85 Wt. % Calcium Hydroxide 15 Wt. % Bentonite ([illegible]) (6)	6.2	12.4	1.3 4.0 6.0	62 57 35	23 0 0	11.7	

(1) For pelleting, all mixtures are blended with 1.0 wt. % [illegible] die lubricant.
(2) 48 hours @ [illegible] hours @ [illegible] hours @ [illegible]
(3) Alcoa C-33 hydrated alumina, 65.0 wt. % Al_2O_3, balance water.
(4) [illegible], 45.5% SiO_2, 38.4% Al_2O_3.
(5) [illegible], 52.5% SiO_2, 44.4% Al_2O_3.
(6) [illegible], 72.5% SiO_2, 15.4% Al_2O_3.

strength of 3.2 kg. The synthetic silicas produced somewhat softer pellets than those obtained with the diatomites. Using 15 wt % of hydrated amorphous silica, the crush strength is 7.4 kg, and with 5% the crush strength is 10.9 kg. With 15 wt % of anhydrous amorphous silica, crush strength is 9.6 kg. Relatively soft pellets (4.8 kg) were obtained using 15 wt % silica derived from a silica colloidal dispersion.

Table III-7 lists test results with combinations of calcium hydroxide and alumina or aluminum silicates. Two formulations with hydrated alumina were prepared corresponding to 5 wt % and 15 wt % Al_2O_3, giving pellets of crush strength 11.0 and 9.3 kg, respectively. These values are slightly higher than those obtained using 5 and 15 wt % hydrated amorphous silica (9.6 and 7.4 kg, respectively), and comparable to values obtained with 5 and 15 wt % uncalcined diatomite (11.0 and 12.8 kg respectively). Very hard pellets were obtained with 17 wt % uncalcined kaolinite (11.4 kg) and 15 wt % bentonite (12.4 kg). Pellets from 15 wt % of calcined kaolinite were softer than those obtained using uncalcined kaolinite (8.6 vs 11.4 kg).

III.3.2.2.3 Use of Portland and Calcium Aluminate Cements

Portland cement and calcium aluminate cement are widely used hydraulic cements consisting of calcium silicates and calcium aluminates. These are fine powders of specified composition and properties, which harden upon mixing with water. We agglomerated powdered calcium hydroxide (or calcium carbonate) by mixing the calcium compound with a minor portion of cement and then blending with water to make a paste.

We selected a Portland Type I cement which consists typically of 44.0% tricalcium silicate, 22.3% dicalcium silicate, 14.3% tricalcium aluminate, and 8.0% tetracalcium aluminoferrite. Calculated CaO content is 61.8%, SiO_2 is 19.4%, and Al_2O_3 is 7.1%. The calcium aluminate cement consists largely of mixed calcium aluminates, mainly monocalcium aluminate. Calculated CaO content is 35.8%, Al_2O_3 + TiO_2 is 44.0% and SiO_2 is 8.6%.

Four wet mixtures were prepared with $Ca(OH)_2$ and commercial hydraulic cements, as shown in Table III-8. The cements consist mainly of calcium silicates and calcium aluminates which may be represented as compositions of CaO, SiO_2 and Al_2O_3. In order to obtain correspondence to other sorbents which contain 15 wt % SiO_2 or Al_2O_3, we chose to base the quantity of cement used in each formulation on the portion of the cement which is not "CaO". For example, Portland Type I cement consists of 61.8 wt % CaO and, by definition, 38.2 wt % "non-CaO". Therefore, a combination consisting of 60.7 wt % calcium hydroxide and 39.3 wt % Portland cement is equivalent to 60.7 wt % calcium hydroxide, 24.3 wt. % CaO, and 15.0 wt % "non-CaO". These four preparations were made using

TABLE III-4

[illegible] CALCIUM HYDROXIDE AND CALCIUM CARBONATE [illegible] PORTLAND CEMENT AND CALCIUM ALUMINATE CEMENT

Composition (1)	Crush Strength of 3.2 cm Pellets, kg		Laboratory Reactor Test: 10,000 v/v/hr., 315°C				Notebook Reference (4)
	Initial	After Heat Treating (2)	Total Exposure To Feed, Hours	H_2S Trapping Efficiency, %	SO_2 Trapping Efficiency, %	Final Crush Strength of Pellets, kg	
48.8 Wt. % Calcium Hydroxide 51.2 Wt. % Portland Type I Cement	5.4	22.9	1.2 4.0 6.0	75 76 78	3 6 3	23.0	60-9
60.7 Wt. % Calcium Hydroxide 39.3 Wt. % Portland Type I Cement	11.2	22.7					90
78.0 Wt. % Calcium Hydroxide 22.0 Wt. % Calcium Aluminate Cement (Alcoa [illegible])	(3)	(3)	1.2 3.7 3.7	85 86 76	21 18 10	(3)	60-10
61.8 Wt. % Calcium Hydroxide 38.2 Wt. % Calcium Aluminate Cement (Alcoa CA-25)	6.8	22.5					91
73.2 Wt. % Calcium [illegible] 26.8 Wt. % Portland Type I Cement	(3)	(3)	1.3 3.8 5.8	66 30 72	0 0 0	(3)	43
60.7 Wt. % Calcium Carbonate 39.3 Wt. % Portland Type I Cement	9.9	22.5					60-1
78.4 Wt. % Calcium Carbonate 21.6 Wt. % Calcium Aluminate Cement ([illegible])	1.8	6.2					60-2
80.0 Wt. % Calcium Carbonate 20.0 Wt. % Calcium Aluminate Cement (Alcoa CA-25)	(4)	(4)					92

(1) For pelleting, all mixtures are blended with 3 wt. % Sterotex. (2) 48 hours @ 95°C/16 hours @ 120°C/16 hours @ 315°C

(3) Tested as 6 mesh chips. Crush strength was not measured. (4) Material could not be pelleted.

32 and 39.3 wt % of Portland Type I cement, 21.0 wt % of Atlas Refcon calcium aluminate cement, and 19.0 wt % of Alcoa CA-25 calcium aluminate cement.

All combinations of calcium hydroxide with Portland cement, and with calcium aluminate cements, produced hard pellets, except for the combination containing 21 wt % Atlas calcium aluminate cement. This combination set to a very hard material, which was judged too hard to be pelleted, so instead was broken into 6-mesh particles for reactor testing. The combinations employing 32.0 and 39.3 wt % Portland cement produced pellets of 11.9 and 12.7 kg crush strength, respectively. Similar pellets were obtained with 19.0 wt % Alcoa calcium aluminate cement (crush strength 11.5 kg).

Calcium carbonate is an alternative to calcium hydroxide for combination with cements. Calcium carbonate has an advantage over calcium hydroxide of undergoing less volume increase upon sulfation (sulfated volume expansion ratio = 1.10 for $CaCO_3$, vs. 1.36 for $Ca(OH)_2$). One mixture of powdered calcium carbonate with 26.8 wt % Portland Type I cement was prepared and made into a wet paste as above. This mixture contained the equivalent of 73.2 wt % $CaCO_3$, 16.6 wt % CaO and 10.2 wt % "SiO_2/Al_2O_3". The paste solidified to a very hard material which was broken up and reactor-tested directly, without being made into pellets. Another mixture with 39.3 wt % Portland cement was also made, as were two mixtures with calcium aluminate cement, at the 23.4 and 19.0 wt % levels. The higher Portland cement level resulted in very hard pellets. The two calcium aluminate mixtures gave unsatisfactory pellets.

III.3.3 Laboratory Reactor Tests of Sorbent Particles

III.3.3.1 Experimental Procedure

Using a laboratory reactor, the experimental sorbents described in Sections III.3.1 and III.3.2 were evaluated for efficiency in trapping $SO_4^=$ and SO_2. Thirteen ml of sorbent (3.2 mm pellets unless otherwise noted) were placed in a 25.4 mm diameter quartz tube reactor. A stream of synthetic exhaust gas containing 12% each of CO_2 and H_2O, 20 ppm SO_2, 5 ppm SO_3, 3% O_2 and balance N_2, was blended through a bank of rotometers, and passed over the sorbent at 100,000 v/v/hr and 370°C. The only exceptions were H_2O and SO_3 vapor, which were added by passing the heated gas through a 0.005 normal solution of H_2SO_4. No H_2, CO, or HC was added to the gas stream, even though provision was made for them, since these components would be present in very small quantities in a real post-catalyst exhaust gas, and should have no effect on sorbent activity. Thermocouples were mounted adjacent to the sorbent bed to allow control and recording of the bed temperature. Trapping efficiencies were calculated from $SO_4^=$ and SO_2 concentrations of the gas stream entering and exiting the reactor bed.

The experimental apparatus is shown schematically in Figure III-1. Analysis of the gas stream for SO_2 and SO_3 was made, before or after the sorbent bed, by means of a TECO UV fluorescence instrument and the Goksoyr-Ross coil. Both methods are described in Appendix C.

III.3.3.2 Experimental Results

Tables III-6 to III-9 list the sorption activities of the 10 candidate materials chosen from the preparations of Sections III.3.1 and III.3.2 on the basis of pelleting properties. These include samples of wet mixtures of $Ca(OH)_2$ with various silicas, aluminas, and aluminum silicates, cement-containing combinations, and dry mixtures of $Ca(OH)_2$ with SiO_2 and/or Al_2O_3. In addition, a new benchmark preparation, of nominal 85 $Ca(OH)_2$/10 SiO_2/5 Na_2O composition was also tested.

III.3.3.2.1 Benchmark Sorbent

As indicated in Table III-6, the benchmark sorbent of nominal composition 85 CaO/10 SiO_2/5 Na_2O trapped 94% of the $SO_4^=$ in the feed gas during the first 2.6 hours of the test. The trapping efficiency fell to 72% after 6.9 hours of the test. In previous tests(1), the $SO_4^=$ trapping efficiency of a similar material, at 480°C and 100,000 v/v/hr was 100% after 8.4 hours. Also, at 480°C but 150,000 v/v/hr, efficiency was 97% after 4.2 hours. Previous to the present test, the benchmark sorbent was run only once at 370°C, and this was at 150,000 v/v/hr, rather than 100,000 v/v/hr, the space velocity now being used. Under those conditions, $SO_4^=$ trapping efficiency was 100% after 2.5 hours and 36% after 4.7 hours. The current $SO_4^=$ trapping efficiencies of 94% after 2.6 hours and 72% after 6.9 hours are roughly comparable to the earlier results at the higher space velocity. The present reactor testing conditions, employing the lower reactor temperature (370°C vs. 480°C), which is more typical of vehicle condition, constitutes a more severe test for experimental sorbents, since the rates for chemical reaction and diffusion through the sorbent may be expected to be lower at the lower temperature.

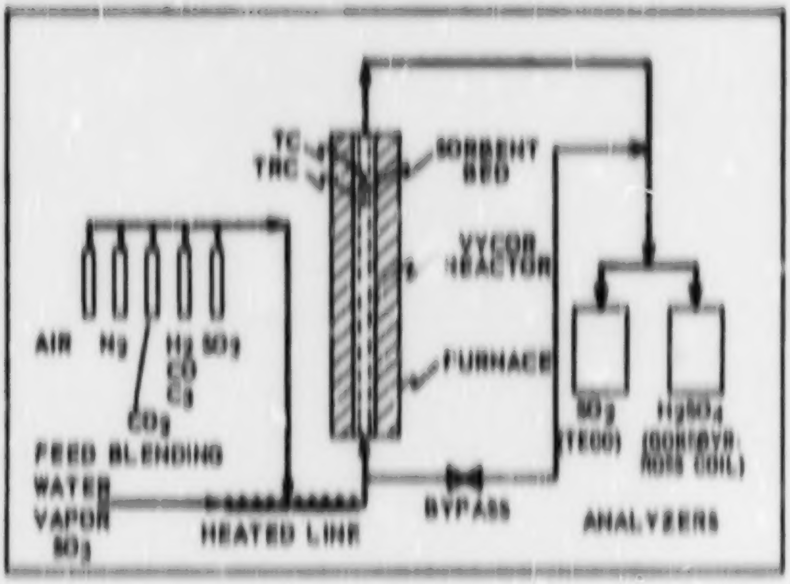
Trapping efficiency for SO_2, as found in the present test, is 33-60% over a period of 6.9 hours, which is similar to sorption levels which have previously been obtained with benchmark sorbent.

III.3.3.2.2 Dry Mixes

As indicated in Table III-9, pellets made from 100% calcium hydroxide are ineffective as a sorbent, giving essentially nil $SO_4^=$ trapping efficiency. Two dry mixtures of calcium hydroxide with silica and with alumina, have also been tested as described in Table III-9. Trapping efficiencies for $SO_4^=$ are 46-60%. As expected for the lack of sodium content in these mixtures, SO_2 trapping efficiency is near zero.

FIGURE III-1

APPARATUS FOR LABORATORY SCREENING OF SORBENTS



(THE BYPASS IS LOCATED AFTER THE WATER VAPOR + SO_3 ARE ADDED.)

TABLE [illegible]

[illegible]

Composition (1)	Crush Strength of 3.2 mm Pellets, kg Initial	Crush Strength of 3.2 mm Pellets, kg After Test Heating (2)	[illegible] Total Exposure to Feed, Hours	[illegible] [illegible] Trapping Efficiency, %	[illegible] [illegible] Trapping Efficiency, %	[illegible] Final Crush Strength of Pellets, kg	[illegible] Reference [illegible]
[illegible]	2.7	4.1	1.2	68	6		33-1
			3.3	46	5	5.3	
[illegible] (3)	3.5	4.5	1.2	65	5		33-2
			3.6	68	8		
			5.6	56	3	4.6	
[illegible]	6.0	8.6	1.3	8	5		34-8
			4.5	39	5		
			7.8	4	5	6.0	
			9.8	2	8		

(1) [illegible]

(2) [illegible]

(3) [illegible]

III.3.3.2.3 Wet Mixes

Only one wet mixture with silica has been reactor tested. This is the combination of calcium hydroxide with 15 wt % uncalcined diatomite which made very hard pills (12.8 kg crush strength). As indicated in Table III-6, $SO_4^=$ trapping efficiency varied from 57-71% over the 5.7 hour test period. Trapping efficiency for SO_2 was only 12-20%. Of the combinations with alumina tested, (see Table III-7) the two mixtures with 7.2 wt % hydrated alumina and 21.6 wt % hydrated alumina were essentially equivalent, giving $SO_4^=$ trapping efficiencies of 83-56% over a six hour period. One aluminum silicate (15% bentonite) was also tested and had similar characteristics (trapping efficiency 63-55% over 6 hours).

III.3.3.2.4 Cements

Only one pelleted cement composition was tested - calcium hydroxide with 32% Portland Type I cement (see Table III-8). The trapping efficiency of this material for $SO_4^=$ was 70-76% over the 6 hour test period. The SO_2 trapping efficiency was near zero. Two cement compositions were tested as 6-mesh chips rather than as pellets. One of these was formulated from calcium hydroxide and 21 wt % Atlas Refcon calcium aluminate cement. Trapping efficiency for $SO_4^=$ of this material was 85-76%. Trapping efficiency for SO_2 was only 23-10%. The other composition tested as chips was made from calcium carbonate with 26.8 wt % Portland cement. Trapping efficiency for $SO_4^=$ of this material was 30-72% and SO_2 trapping efficiency was near zero.

III.3.3.2.5 Discussion of Experimental Results

None of the experimental sorbents described above were as efficient in trapping $SO_4^=$ as the benchmark sorbent. This may in part be due to a beneficial effect due to the sodium component in the benchmark sorbent. Also, because many of the materials produce such hard pellets, the resultant porosity may be low. Later sections will describe attempts to increase porosity through such techniques as calcining, use of burn-out agents and pellet compaction to lower density levels.

III.3.4 Effect of Heat Treatment and Compaction on Pellets

III.3.4.1 Temperature Effects on Pellet Strength

A brief study was undertaken to determine the optimum temperature for heat treating pelletized trap material. These studies were carried out with the benchmark sorbent 85 CaO/10 SiO_2/5 Na_2O, which had been made into 3 mm pellets after drying at 65°C.

Heat treatment drives off excess water and conditions the pellets to temperatures that will be encountered in service. These temperatures may be expected to range from 260-480°C. We also wanted to know if greater pill strength can be achieved by calcining at much higher temperatures.

In three test series, pellet samples were exposed to progressively greater temperatures up as high as 1100°C. After each temperature interval, a sample of pellets was removed and tested for crush strength. The data from these tests is given in Table III-10.

Over the temperature range studied for this particular composition, there was an optimum temperature range for pellet strength at 260-315°C. In this temperature range, crush strength reached a maximum of 7.3-7.7 kg. Crush strength decreased to below 3 kg above 425°C, and to 1.5 kg at 565°C.

It was found that calcining 5 hours at 540°C removes essentially all water of hydration and converts calcium hydroxide to calcium oxide. However, at 315° most of the calcium remains in the form of calcium hydroxide. The equilibrium vapor pressure for water with calcium hydroxide is 100 mm at 300°C and 760 mm at 512°C. It appears that dehydration of calcium hydroxide above 315°C in the oven test is one reason for loss of crush strength.

Another possible explanation is loss of water from calcium silicate hydrates, which decompose between 300-800°C. Hydrated calcium silicates form a gel-like structure which is a primary binding component of materials such as Portland Cement. Probably such a structure contributes to the strength of pellets of this composition.

Although loss of crush strength above 315°C has been demonstrated under dry oven conditions, it is expected that in a vehicle, where exhaust gas contains ~12% water, higher temperatures are allowed without deterioration because of the equilibrium of water vapor with hydrated sorbent.

III.3.4.2 Compaction Effects on Pellet Strength and Sorption Activity

In order to investigate the effects of pelleting to lower crush strengths, and heat treating at 650°C, three batches of pellets were made from one preparation of 85 $Ca(OH)_2$/15 Diatomite, having different crush strengths, by varying the compacting conditions. As listed in Table III-11, the weakest pellets, Batch 1, were made to an initial crush strength of 3.9 kg. After heat treating at 315°C, these pellets had a crush strength of 5.0 kg and density of 1.25 g/cm³. A

TABLE III-10

The Effect of Heat Treatment Conditions on Pellet Crush Strength(1)

Temperature °C	Series 1 Hrs. @ Temp.	Series 1 Crush Strength kg	Series 2 Hrs. @ Temp.	Series 2 Crush Strength kg	Series 3 Hrs. @ Temp.	Series 3 Crush Strength kg
65	64	6.6 (2)	64	6.6 (2)	64	6.6 (2)
95	↓	↓	66	5.6	65	(3)
150	↓	↓	8	5.5	8	(3)
205	↓	↓	↓	↓	↓	↓
260	↓	↓	↓	↓	16	7.7
315	↓	↓	16	7.3	↓	↓
370	↓	↓	↓	↓	8	5.2
425	↓	↓	↓	↓	16	2.8
455	↓	↓	8	3.7	↓	↓
480	↓	↓	↓	↓	16	2.3
540	5	2.2	↓	↓	-	-
595	-	-	16	1.5	-	-
1100	-	-	8	1.1	-	-

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(1) The above data are for 3-mm pellets produced from 85 [illegible]/5 Na₂O sorbent which had been dried 64 hours @ 65°C prior to granulating and pelletizing. Notebook references 4349-4, 12, 13.

(2) These are initial crush strengths for the sorbent after pelletizing.

(3) No sample was taken for crush strength.

TABLE III-11

PREPARATION OF 85 $Ca(OH)_2$/15 [illegible] PELLETS OF DIFFERENT CRUSH STRENGTHS WITH HEAT TREATING AT [illegible]

Heat Treatment After Pelleting	3.2 mm Pellets (1)					
	Batch 1		Batch 2		Batch 3	
	Crush Strength, kg	Density g/cm^3	Crush Strength, kg	Density g/cm^3	Crush Strength, kg	Density g/cm^3
None	2.9	—	5.8	—	7.8	—
16 h @ 95°C 6 h @ 150°C 16 h @ 315°C	5.0	1.25	8.3	1.36	11.6	1.40
16 h @ 95°C 6 h @ 150°C 16 h @ 315°C 2 h @ 540°C 4 h @ 650°C	3.3	1.39	6.3	1.29	8.5	1.35

(1) Notebook Reference 4349-138. The different original crush strengths were obtained from one preparation of sorbent by using three different [illegible] settings during pelleting, i.e., low [illegible] produces softer pellets.

portion of these pellets was further heated at 650°C, giving pellets of crush strength 3.3 kg, and density 1.19 g/cm^3. Of the heat treated pellets, these had the lowest crush strength and the lowest density. As shown in Table III-12, these also had the highest $SO_4^=$ trapping efficiency yet obtained for sorbents of this composition (81-73% over 11.7 hours). The pellets heat treated at 315°C were only slightly lower in efficiency (84-60% over 9.4 hours). Previous pellets of this sorbent made at higher crush strength (13.5-12.8 kg) and higher density (1.58-1.71 g/cm^3) had lower $SO_4^=$ trapping efficiencies (71-15% over 11.3 hours). The lower activity of the pellets having higher crush strength and higher density was probably a consequence of lower porosity and smaller pores. It is apparent that a compromise has to be made between crush strength and porosity, so as to obtain pellets having both adequate mechanical strength and activity.

III.3.5 Increased Pellet Porosity

III.3.5.1 Pore Volume and Surface Area Relationship

Table III-13 lists pore volume, surface area, and density measurements on pellets of benchmark sorbent and pellets made from 100% calcium hydroxide. In the laboratory reactor screening test, benchmark sorbent was much more effective at sorbing $SO_4^=$ than was 100% $Ca(OH)_2$ sorbent (94-72% trapping efficiency vs. 0-20%). Referring to Table III-13, the superior trapping efficiency of benchmark sorbent is associated with higher pore volume (0.236 vs. 0.142 ml/g) and lower density (1.407 vs. 1.744 g/cm^3) relative to 100% $Ca(OH)_2$ sorbent. However, total surface area is less for benchmark sorbent (8.5 vs 16.3 m^2/g). The surface area is less even though total pore volume is higher, because most of the pore volume occurs in large pores. This is apparent from a distribution analysis of pore volume and surface area versus pore size. Considering pore sizes in the range of 25-1200 Å, benchmark sorbent has 99% of its porosity in pores of 200-1200 Å, and 75% in pores of 600-1200 Å. However, 100% $Ca(OH)_2$ sorbent has 38% of its porosity in pores of 25-200 Å, and only 19% in pores of 600-1200 Å. Consequently, 93% of the surface area in benchmark sorbent occurs in pores of 200-1200 Å, with 55% in the 600-1200 Å range. This analysis only covers pores up to 1200 Å. Because in the case of benchmark sorbent there is a sizable contribution to pore volume by the largest pores in this range, we may expect that significant pore volume and surface area also exists due to pores larger than 1200 Å. In contrast, 100% $Ca(OH)_2$ sorbent has 74% of its surface area in pores of 25-200 Å, 45% in the smallest pores of 25-100 Å, and only 4% in pores above 600 Å. The reactivity of benchmark sorbent is apparently a result of substantial porosity in the 600 + Å size range. As discussed in the following sections, this information was applied to the design of potentially more efficient sorbents. Additional studies on the relationship of sorbent physical properties and sorption activity may be found in Section III.7.

TABLE III-12

85 Ca(OH)2 /15 [illegible] SORBENT
EFFECTS OF CRUSH STRENGTH AND HEAT TREATING ON DENSITY AND ACTIVITY

Heat Treating Conditions	Density g/cm³	Crush Strength (kg) Initial	Crush Strength (kg) After Reactor Test	Laboratory Reactor Screening Test 20,000 v/v/hr, 30°C: Total Exposure To Feed Gas, Hours	CH3I* Trapping Efficiency, %	I2 Trapping Efficiency, %	Notebook Reference
48 h @ 95°C	1.71	12.0	11.5	1.3	57	20	4369-60-1
6 h @ 150°C				3.7	71	12	
16 h @ 315°C				5.7	62	12	
48 h @ 95°C	1.50	12.5	11.6	1.3	70	31	4369-60-2
6 h @ 150°C				3.6	36	25	
16 h @ 315°C				5.4	28	28	
5 h @ 540°C				6.7	23	26	
				9.3	16	26	
				11.3	12	25	
16 h @ 95°C	1.25	5.0	7.8	1.3	83	16	4369-130-1
6 h @ 150°C				3.3	86	19	
16 h @ 315°C				4.5	77	16	
				7.4	60	11	
				9.6	63	8	
16 h @ 95°C	1.19	3.3	5.3	1.6	78	32	4369-130-2a
6 h @ 150°C				3.9	91	21	
16 h @ 315°C				5.9	88	16	
2 h @ 540°C				7.2	82	12	
4 h @ 650°C				9.7	76	8	
				11.7	73	8	

TABLE III-11

PORE VOLUME, SURFACE AREA AND DENSITY OF SORBENTS VS. $SO_4^=$ TRAPPING EFFICIENCY

	Benchmark Sorbent "85 CaO/10 SiO_2/5 Na_2O"(1)	100% $Ca(OH)_2$(1)
Pore Volume, ml/g	0.238	0.142
Surface Area (BET) sq. m./g	8.5	16.3
Pore Volume Distribution, %(2)		
25- 100 Å	0.2	15.1
100- 200 Å	1.2	22.0
200- 600 Å	23.6	43.9
600-1200 Å	75.0	19.1
Surface Area Distribution, %(2)		
25- 100 Å	2.3	45.4
100- 200 Å	5.3	28.2
200- 600 Å	37.6	22.7
600-1200 Å	54.7	3.7
Density, g/cm^3	1.407	1.744
$SO_4^=$ Trapping Efficiency, %	94-77	0-20

(1) 3.2 mm pellets heat treated 16 hours at 315°C.

(2) Pore volume and surface area distributions are for pore sizes in the range of 25 - 1200 Å. Contributions from pores larger than 1200 Å are not included in these analyses, although contributions from these may be appreciable for the benchmark sorbent.

III.3.5.2 Heat Treating

In an initial attempt to increase $SO_4^=$ trapping efficiency by increasing porosity, nine samples of pelleted sorbents were heated at 540°C, with the intent to dehydrate $Ca(OH)_2$ to CaO. The vapor pressure of water due to dissociation of $Ca(OH)_2$ at 540°C is approximately 180 kPa (1.75 atmospheres). At 512°C the pressure is 101 kPa (1 atmosphere). We had previously decided to limit heat treatment of pelleted sorbents to 315°C so as to avoid dehydration of $Ca(OH)_2$ while obtaining maximum crush strength. As discussed in Section III.3.4.1 crush strength of benchmark sorbent reaches a maximum at 315°C and decreases at higher temperatures. Consequently, we were concerned with the effect of heat treating on crush strength as well as the effect on porosity and reactivity.

Table III-14 lists inspections on six samples of pellets which were heat treated at 540°C after initial treatment at 315°C. As expected, the crush strength of benchmark sorbent was much reduced - from 8.8 kg to 2.6 kg. Less severe reductions in crush strength occurred with the other sorbents. Pellets made from a wet mixture of 15 wt % uncalcined diatomite in calcium hydroxide experienced the least loss in crush strength (12.8 kg vs. 12.5 kg). All pellet samples decreased in density by as much as 11% as a result of weight loss. Essentially no change occurred in pellet dimensions. The weight loss was only half (or less) that which would be expected if all the $Ca(OH)_2$ were converted to CaO. Apparently, much of the water bound to calcium in pelleted sorbents is more tightly bound than is water in pure $Ca(OH)_2$. An alternate explanation is that the pellets are insufficiently porous but sufficiently strong to contain water vapor in excess of one atmosphere internal pressure.

Three of these sorbents were tested for $SO_4^=$ trapping efficiency in the laboratory reactor. In Table III-15 are listed $SO_4^=$ and SO_2 trapping efficiencies for benchmark sorbent, 85 $Ca(OH)_2$/15 diatomite sorbent, and 78.4 $Ca(OH)_2$/21.6 hydrated alumina sorbent. Results are given for pellets tested after heating at 315°C (our previous heat treating temperature) and after heating at 540°C. There is no increase in $SO_4^=$ trapping efficiency of any of these sorbents as a result of heating at the higher temperature. In the case of the diatomite and hydrated alumina preparations, $SO_4^=$ trapping efficiencies appear to have decreased slightly, and SO_2 trapping efficiencies have increased. The SO_2 trapping efficiency of the alumina-containing sorbent has increased from 0 to 30-49%. Based on these results, and the pore volume/surface area measurements discussed in the preceding section, it is concluded that heating at 540°C does not produce the large pores which are apparently required for adequate $SO_4^=$ trapping efficiency.

TABLE III-14

EFFECT OF HEAT TREATING AT 315°C AND 540°C ON CRUSH STRENGTH AND DENSITY OF PELLETED SORBENT COMPOSITIONS

Composition (3.2-mm pellets)	Crush Strength (kg)		Density, g/cm^3		Notebook Reference 4368
	315°C[1]	540°C[2]	315°C	540°C	
Benchmark 85 CaO/10 SiO$_2$/5 MgO	6.8	2.6	1.407	1.279	60-11
100% Ca(OH)$_2$	9.9	7.3	1.744	1.648	60-12
85 wt. % Ca(OH)$_2$ 15 wt. % Diatomite (uncalcined)	12.8	12.5	1.716	1.577	60-1
78.4 wt. % Ca(OH)$_2$ 21.6 wt. % Hydrated alumina	9.6	6.9	1.683	1.531	60-4
83 wt. % Ca(OH)$_2$ 17 wt. % Kaolinite (uncalcined)	11.4	10.8	1.709	1.540	60-7
68 wt. % Ca(OH)$_2$ 32 wt. % Portland Type I Cement	11.9	8.5	1.735	1.600	60-9

(1) After 16 hours at 315°C.
(2) Pellets which had been heated 16 hours at 315°C were further heated 5 hours at 540°C.

TABLE III-15

$SO_4^=$ AND SO_2 TRAPPING EFFICIENCIES OF PELLETS HEAT TREATED AT 540°C VS. EFFICIENCIES AFTER HEAT TREATING AT 315°C

			Laboratory Reactor Screening Test: 100,000 v/v/hr., 370°C				
			Pellets After Heat Treating @ 315°C		Pellets After Heat Treating @ 540°C		
Composition	% Change In Density After Heating 5 Hours @ 540°C (1)	Total Exposure To Feed Gas, Hours	$SO_4^=$ Trapping Efficiency, %	SO_2 Trapping Efficiency, %	$SO_4^=$ Trapping Efficiency, %	SO_2 Trapping Efficiency, %	Notebook Reference 4300
Benchmark Sorbent "85 CaO/10 SiO$_2$/5 MgO"	-9.1%	0.9	—	—	95	79	44
		1.3	94	60	—	—	
		2.6	94	40	—	—	
		3.1	—	—	99	64	
		5.3	—	—	81	58	
		6.6	—	—	73	57	
		6.9	72	33	—	—	
		8.9	—	—	67	43	
		10.9	—	—	63	43	
		12.2	—	—	50	42	
		15.4	—	—	45	42	
		17.4	—	—	54	39	
85 Wt. % Calcium Hydroxide 15 Wt. % Diatomite (uncalcined) (Dicalite 583)	-8.0%	1.3	57	20	70	31	60-1
		3.6	—	—	36	25	
		3.7	71	12	—	—	
		5.4	—	—	28	28	
		5.7	52	12	—	—	
		6.7	—	—	23	16	
		9.3	—	—	14	25	
		11.3	—	—	12	26	
78.4 Wt. % Calcium Hydroxide 21.6 Wt. % Hydrated Alumina (Alcoa C-330)	-9.0%	1.2	—	—	67	49	60-4
		1.3	83	0	—	—	
		3.2	—	—	51	43	
		3.5	55	—	—	—	
		4.5	—	—	45	30	
		6.8	56	0	—	—	
		7.4	—	—	33	38	
		9.4	—	—	30	36	

(1) The density of 3.2 mm pellets which were initially heat treated at 315°C was remeasured after heat treating at 540°C.

III.3.5.3 Blowing Agents

Sorbent preparations discussed in previous sections have had inadequate reactivity for $SO_4^=$, apparently because pores are too small. In an initial attempt to generate large pores, compositions of 85 $Ca(OH)_2$/15 diatomite were prepared using 5 and 10 wt % of added cellulose fibers, of three different sizes (50-60 μm, 100-140 μm, and 290 μm in length). Of these compositions, only those containing 5 and 10 wt % of the smallest cellulose fibers (50-60 μm) were successfully pelleted, although the 10% composition had to be pelleted in two passes, i.e., soft pellets were made which were reground and repressed to make satisfactory pellets. The resulting pellets were heated at 540°C for 70 hours to burn off the cellulose fibers. In Table III-16 are listed crush strengths and densities of these pellets vs. those properties obtained with sorbent without cellulose, and with benchmark sorbent. As a result of incorporation of cellulose fibers, crush strengths were reduced from 11.5 kg (without cellulose) to 8.6 and 6.5 kg for 5 and 10% cellulose, respectively. These crush strengths were still satisfactory. Densities decreased as a result of weight loss from 1.714 g/cm³ (without cellulose) to 1.379 and 1.407 with 5 and 10% cellulose, respectively. These are the lowest densities which we have measured for pellets of other than benchmark composition. The decrease in density due to 5% cellulose is 20%. It was surprising that the higher level of cellulose did not provide even lower density; however, this was probably a result of the different compacting conditions.

Laboratory reactor tests for the sorbent made with 5% cellulose, vs. that without cellulose, are given in Table III-17. After ~3.5 hours on test, the difference in $SO_4^=$ sorption efficiencies of the two sorbents is 20-25%, with the cellulose composition having the higher efficiency. However, even these efficiencies are 20-30% lower than those obtained with benchmark sorbent.

A wet mixture preparation of $CaO/SiO/Na_2O$ plus 10% cellulose after burn-out of cellulose showed $SO_4^=$ trapping efficiency almost as good as benchmark sorbent prepared by the coprecipitation method (Table III-18). The sorbent's trapping efficiency during a 10 hour evaluation ranged from 90 to 77%. However, its SO_3 trapping efficiency was high, 69-33%. The inclusion of cellulose and then burn-out apparently helped improve the sorbent's porosity and activity. A previous wet mixture of $CaO/SiO/Na_2O$ had shown much poorer $SO_4^=$ trapping efficiency: 72-55%.

The sorbent was prepared by mixing the dry ingredients together and then sufficient water was added to make a paste. The material was dried at 65°C and granulated to 14-40 mesh and pressed into 3.2 mm pellets. The $CaO/SiO/Na_2O$ + 10% cellulose was heat treated in a Vycor reactor in a tube furnace, initially at 340°C under nitrogen, then in air and the

TABLE III-16

CRUSH STRENGTH AND DENSITY OF PELLETED SORBENTS

Composition (3.2-mm pellets)	Hours at 540°C.	Average Crush Strength [illegible]	Average Density g/cm³	Notebook Reference 4099
Benchmark 85 CaO/10 SiO_2/5 Na_2O	5	2.6	1.279	68-21
85 wt. % $Ca(OH)_2$ 15 wt. % Diatomite (uncalcined)	5	12.5	1.577	68-1
85 wt. % $Ca(OH)_2$ 15 wt. % Diatomite (uncalcined) plus 5 wt. % Solka-Floc BW-40 (Cellulose Fibers)	70	8.6	1.379	122-2
85 wt. % $Ca(OH)_2$ 15 wt. % Diatomite (uncalcined) plus 10 wt. % Solka-Floc BW-40 (Cellulose Fibers)	70	6.5	1.407	122-1

TABLE III-17

SO$_4^=$ AND SO$_2$ TRAPPING EFFICIENCIES OF PELLETED SORBENTS

Composition (3.2-mm Pellets)	Crush Strength (kg) Initial (After 540°C)	Crush Strength (kg) After Reactor Test (370°C)	Laboratory Reactor Screening Test: 100,000 v/v/hr., 370°C Total Exposure To Feed Gas, Hours	SO$_4^=$ Trapping Efficiency, %	SO$_2$ Trapping Efficiency, %
Benchmark Sorbent: "85 CaO/10 SiO$_2$/5 MgO" RB-4349-46 Actual MgO content = 4.5% Heat treated 5 hrs. @ 540°C	2.6	6.8	0.9	95	53
			3.1	68	38
			5.3	81	32
			6.6	73	31
			8.9	67	27
			10.9	63	27
			12.2	50	16
			15.4	45	26
			17.4	56	13
85 wt. % Calcium Hydroxide 15 wt. % Diatomite (uncalcined) (Dicalite SA3) RB-4349-48-1 Heat treated 5 hrs. @ 540°C	12.5	11.6	1.3	70	5
			3.4	34	0
			5.4	28	2
			6.7	23	0
			9.3	24	0
			11.3	12	0
85 wt. % Calcium Hydroxide 15 wt. % Diatomite (uncalcined) (Dicalite SA3) plus 5 wt. % added 30-40 μm Cellulose Fibers (Solka-Floc BW-40) RB-4349-120-2 Heat treated 70 hrs. @ 540°C	8.6	7.7	1.3	80	23
			3.5	57	17
			4.8	53	15
			9.3	46	18
			10.5	35	12
			15.3	-2	15

TABLE III-18

EVALUATION OF SORBENTS IN THE LABORATORY SCREENING TEST

Composition	Final Heat Treating Conditions	Density g/cm³	Crush Strength, kg		Laboratory Reactor Screening Test 100,000 v/v/h, 370°C		
			Initial	After Reactor Test	Total Exposure To Feed Gas, Hours	SO_3 Trapping Efficiency, %	SO_2 Trapping Efficiency, %
CaO/SiO₂/Na₂O + 10% Cellulose (80/10/10) (RD 4269-126)	3 hrs @ 540°C	1.28	4.2	8.2	1.0	90	69
					3.0	78	47
					5.0	87	47
					6.8	78	39
					8.0	73	33
					10.8	77	33
$Ca(OH)_2$ + Ludox HS (70/30) (RD 4269-71)	16 hrs @ 315°C	1.40	4.8	6.1	1.0	56	26
					3.8	49	18
					6.8	46	31
					6.8	45	25
					11.6	26	25
Carbon (Calgon) Sample A			>13.5	11.9	1.0	62	3
					3.0	70	14
					5.5	65	3
					6.5	59	11
					8.6	60	8
					11.6	65	11
Sample B			13.5	11.0	1.3	55	0
					3.8	50	3
					4.8	73	5
					5.8	63	3
					9.2	76	0

temperature was gradually raised to 540°C and maintained at 540°C for three hours. The burn-out of the cellulose was judged complete when all the grey coloration of the pellets disappeared.

In Table III-19 are listed data obtained with four preparations of 85 $Ca(OH)_2$/15 diatomite made with the following cellulose or starch additions: (1) no addition, (2) 5 wt % of 50-60 μm cellulose fibers, (3) 10 wt % of 25 μm cellulose fibers, (4) 10 wt % of starch, and (5) 20 wt % of starch. Although in general, densities were lower as a result of burning out the starch or cellulose components, $SO_4^=$ trapping efficiencies were not improved as much as desired. Further, inspection of density data before and after burn-out indicated that overall shrinkage of pellets could be significant over the extended burn-out times employed (70-120 hours). In one case, pellet shrinkage was sufficient to result in a net density increase after burning out a cellulose or starch component. The last preparation in Table III-19, which was made with 20% starch, was heat treated for 16 hours at 315°C and then for 71 hours at 540°C. The average pellet height decreased from 3.21 mm (after 315°C) to 3.08 mm, (after 540°C), diameter decreased from 3.16 to 3.09 mm, and weight decreased from 35.3 to 32.6 mg. As a result of combined shrinkage and weight loss, the density after burn-out at 540°C was actually slightly greater (1.41 g/cm^3) than the density after 315°C (1.40 g/cm^3). It is likely that such shrinkage is closing the large pores generated by the burn-out procedure, although no actual pore size analyses are available.

III.3.6 Effect of Sodium on Sorbent Activity

One of our intentions in preparing sorbent formulations has been to avoid use of sodium so as to minimize sorption of SO_3. It appears, however, that some sodium may be required in order to obtain high $SO_4^=$ trapping efficiency. Moreover, we have found that elimination of sodium does not entirely eliminate SO_3 sorption, and that Na_2O content on the order of 5-7% may be tolerable in this respect.

III.3.6.1 Sodium Content of Benchmark Sorbent

In Table III-20 are listed reactor test results for two preparations of "85 CaO/10 SiO_2/5 Na_2O" benchmark sorbent, each tested two times. These two preparations differed in actual sodium content (as a result of different wash procedures) and also in $SO_4^=$ trapping efficiency. The first preparation contained 4.5 wt % equivalent Na_2O content. Its $SO_4^=$ trapping efficiency was 95-56% over 17.6 hours. The second preparation, which contained 7.5 wt % equivalent Na_2O had trapping efficiencies of 97-85% over 18.2 hours. After 48 hours on test, SO_3 trapping efficiencies were below 30%.

TABLE III-19

[illegible]

Composition [illegible]	Final Heat Treating Conditions	Density g/cc	Crush Strength, lb: Initial	Crush Strength, lb: After Reactor Test	Laboratory Reactor Screening Test [illegible]: Total Exposure To Feed Gas, Hours	Trapping Efficiency, %	Trapping Efficiency, %
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]
[illegible](1)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]
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					[illegible]	[illegible]	[illegible]
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					[illegible]	[illegible]	[illegible]
[illegible](2)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]		NOT EVALUATED IN SCREENING TEST		

(1) See also Table [illegible]

(2) See also Table [illegible]

TABLE III-28

REACTOR TESTS OF "[illegible]" [illegible]

Notebook Reference	Equivalent MgO Content %	Heat Treating Conditions	Crush Strength, kg Initial	Crush Strength, kg After Reactor Test	Laboratory Reactor Screening Test 18,000 v/v/h, 200°C Total Exposure To Feed Gas, Hours	[illegible]* Trapping Efficiency, %	[illegible] Trapping Efficiency, %
4249-46	4.5	16 h @ 325°C	4.8	—	1.3	96	60
					2.6	96	40
					6.9	72	37
4249-46	4.5	16 h @ 325°C 6 h @ 540°C	2.6	6.8	0.9	95	55
					3.1	88	38
					5.3	81	32
					6.6	73	31
					8.9	67	17
					10.9	62	17
					12.2	58	16
					15.4	45	16
					17.4	59	13
4249-128	7.5	16 h @ 325°C	12.7	11.3	1.2	93	39
					2.6	95	23
					3.6	97	6
					6.8	96	9
					9.5	96	8
					11.5	93	3
					12.3*	91	20
					18.3*	85	6
4249-128	7.5	16 h @ 325°C	12.2	13.6	2.6	92	41
					4.3	93	27
					5.6	96	39
					8.3	95	32
					10.3	98	29

* Raised reactor temperature to 300°F.

III.3.6.2 Sodium Content of Other Sorbents

Another example of the effect of sodium content on trapping efficiency is given in Table III-21. Two preparations of "$(CaO)_3 (SiO_2 Al_2O_3)_{1/2}$" contained, respectively, 14.6 and 0.5 wt % equivalent Na_2O. Again, the sorbent having the higher level of sodium had the higher $SO_4^=$ trapping efficiency (94-90% vs. 84-45% over 11 hours). Trapping efficiencies for SO_2 were 32-21% for the sorbent containing 0.5% Na_2O, and 61-42% for the sorbent containing 14.6% Na_2O.

III.3.7 Effect of Pore and Surface Area Properties on Sorption Efficiency

A variety of pelleted sorbents, covering a range of activities for sorption of $SO_4^=$, were analysed for pore volume, pore size distribution and surface area. These analyses were obtained by the mercury penetration method run to 24,000 psi. A summary of the data are reported in Table III-22 and also included for comparison are other laboratory test results: heat treating conditions; crush strength; and $SO_4^=$ trapping efficiency.

The results showed that as the crush strength of the pellets increased, directionally the pore volume above 500 Å and the surface area decreased. The data also showed that an increase in porosity probably helps $SO_4^=$ sorption, but is not the only controlling factor. Apparently, the pore structure affects the selectivity, however, the results suggest that the activity of various components of the sorbent is an important variable. The Na_2O in many of the sorbents prepared improved the $SO_4^=$ sorption. Unfortunately, it also improved SO_2 sorption.

III.3.8 Chemical Analysis of Used Sorbents

III.3.8.1 Rings from Vehicle Testing

As part of Modification I of this contract, a vehicle durability test had been performed on benchmark sorbent fabricated into rings having the dimensions 15.9 mm O.D., 5.6 mm I.D., and 7.9 mm height(1). The test was discontinued in March, 1975, after 20 400 kilometers accumulation, because of unsatisfactory $SO_4^=$ trapping efficiency. Subsequently, in June, the trap was removed from the vehicle and cut open. The rings were still intact, although highly compacted and seemingly "cemented" together. The rings were hard, and there was very little fines. Volume expansion of individual rings was estimated to be ~30%. The opened trap was stored loosely covered until samples were to be taken for analysis. After standing five weeks, the hard rings had become very soft, which made sampling of individual rings very difficult. Samples were taken from the inlet area of the trap and from the exit area. A few intact rings were obtained from the middle of the trap. Samples of fresh rings and rings from the trap were analysed for $Ca(OH)_2$, $SO_4^=$, and $CO_3^=$.

TABLE III-[illegible]

[illegible]
[illegible]

Nominal Composition (1)	Equivalent Na₂O Content Wt. % (2)	Crush Strength (kg)		Laboratory Reactor Screening Test [illegible]		
		Initial (After 315°C)	After Reactor Test (370°C)	Total Exposure To Test Gas, Hours	[illegible] Trapping Efficiency, %	[illegible] Trapping Efficiency, %
"[illegible]" [illegible]	8.5	4.8	7.0	1.3	86	32
				1.8	33	21
				6.1	75	32
				9.0	56	38
				11.0	45	38
"[illegible]" [illegible]	24.6	5.0	7.8	2.4	90	61
				4.4	97	56
				5.8	96	53
				8.5	96	42
				10.5	96	42

(1) 3.2 mm pellets heat treated 16 h @ 315°C

(2) Analysis after calcining 5 h @ 815°C by emission spectroscopy.

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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The results of these analyses are given in Table III-23. The analyses for $SO_4^=$ and $CO_3^=$ are given in terms of wt % $CaSO_4$ and wt % $CaCO_3$, although Na_2SO_4 and Na_2CO_3 are certainly also present. The fresh rings contained 58 wt % $Ca(OH)_2$ and 11 wt % $CaCO_3$, the latter arising by sorption of CO_2 from the air during preparation and storage. The used rings from the inlet and exit sections of the trap contained only 2% $Ca(OH)_2$. The concentrations of $CaSO_4$ in the inlet and exit samples were 17% and 12%, respectively. Because of the very low $Ca(OH)_2$ concentrations versus the much higher $CaSO_4$ concentrations, the softening of the rings during storage was probably due to hydration (and consequent expansion) of $CaSO_4$ (or Na_2SO_4) rather than to hydration of any CaO which may have been present in the trap. Equivalent $CaCO_3$ contents for the inlet and outlet samples were found to be 36 and 57 wt %. The lower analysis for these three Ca compounds for the inlet rings may be due to the presence of unanalyzed CaO and/or $CaSiO_3$. The higher inlet temperature would make these more likely than at the trap outlet.

Several intact rings were scraped to obtain samples from the outer surface, the inner surface, and the interior 1/3 of the rings. The $SO_4^=$ concentrations (expressed as $CaSO_4$) of samples from the outer and inner surfaces were 13.8% and 12.6%, respectively. The concentration in the interior of the rings was 9.7%. These data demonstrate that significant $SO_4^=$ collection occurred in the interior portion of the ring, as was found previously with 3.2 mm pellets(1).

The bulk concentration of $CaSO_4$ in the rings, 12-17% after 20 400 km, was much less than the concentration (35%) previously found in the 3.2 mm pellets after 42 400 km(1). Although the degree of sulfation was lower for the rings, $SO_4^=$ sorption efficiency was much inferior, for example, ~30% for the rings at 15 000 km, vs. >95% for the pelleted material. The low trapping efficiency was most likely associated with the much lower geometric surface area of the ring bed relative to 3.2 mm pellets.

III.3.8.3 Pellets from Laboratory Testing

The data obtained with the used rings were very similar to those obtained with 3.2 mm pellets after laboratory reactor tests using synthetic exhaust gas. The fresh pellets were found to contain 53% $Ca(OH)_2$, nil $CaSO_4$, and 23 wt % $CaCO_3$. After the reactor test, the pellets contained only 5% $Ca(OH)_2$, 2% $CaSO_4$, and 72% $CaCO_3$. These data demonstrate that the calcium hydroxide component of such sorbent compositions reacted rapidly and essentially completely with CO_2 from the exhaust gas, and was converted to $CaCO_3$, which became the active component for reacting with $SO_4^=$.

For the pelleted sorbent, 76-79% of the composition was accounted for as $Ca(OH)_2$, $CaSO_4$, and $CaCO_3$. For a nominal 85 CaO/10 SiO_2/5 Na_2O composition, approximately 87% $Ca(OH)_2$ (or 89% $CaCO_3$) is expected. This left approximately 10% of $Ca(OH)_2$ (or $CaCO_3$) unaccounted for, which presumably was present as calcium silicates and/or CaO.

TABLE III-13

ANALYSIS OF BENCHMARK SORBENT (85 CaO/10 SiO₂/5 MgO) OF RINGS AFTER VEHICLE TEST AND OF PELLETS AFTER LABORATORY REACTOR TEST

Analysis	Fresh Rings[1] (Heat Treated 675°C)	Used Rings (20 400 km) Inlet Sample	Used Rings (20 400 km) Exit Sample	Fresh 3.2-mm Pellets (Heat Treated 315°C)	Used 3.2-mm Pellets (After 6.5 hr. in Reactor Test)
Wt. % $Ca(OH)_2$ [2]	58	2	2	53	5
Wt. % $CaSO_4$ [3]	—	17	22	0	2
Wt. % $CaCO_3$ [4]	11	36	57	23	72
Total	69	55	81	76	79

[1] The dimensions of the rings are: outside diameter = 15.9 mm, inside diameter = 5.6 mm, height = 7.9 mm.

[2] Determined by thermal gravimetric analysis from weight loss between 400 and 650°C.

[3] Gravimetric analysis of total $SO_4^=$ expressed as $CaSO_4$.

[4] Analysis of CO_2 by titration expressed as $CaCO_3$.

III.3.9 Other Sorbents

III.3.9.1 Carbon Pellets

Three samples of specially prepared carbon pellets obtained from Calgon Corporation were evaluated in a laboratory screening test. The porosity of these samples were: Sample A, 0.1 ml/g; Samples B and C 0.25 ml/g. Sample C was a modification of Sample B with a reduction in ash content. The pellets were 4.19 mm O.D. and ranged in length from about 4 to 10 mm. The $SO_4^=$ results on Samples A and B are summarized in Table III-18. They could trap some $SO_4^=$, about 65-74%, with little reaction with SO_2, but overall were not as effective as the benchmark sorbent. Sample C showed a 70% reduction in $SO_4^=$, as shown in Table III-25, during a ten hour laboratory test which was run at 370°C and a space velocity of 100,000 v/v/h. These carbon pellets also showed very little SO_2 sorption. The synthetic exhaust gas contained 12% each of CO_2 and H_2O, 20 ppm SO_2, 5 ppm SO_3, 3% O_2, and the balance N_2.

The carbon pellets, Sample C, were further evaluated to determine their practical application. One major potential problem with the use of carbon as a sorbent-reductant is its capacity for oxidation. The burn-off rate on the specially prepared Sample C was measured at 316°C (600°F) and 371°C (700°F). The feed gas contained 12% CO_2 and H_2O, 3% O_2, and the balance nitrogen. A summary of the burn-off rates follows:

Table III-26

Carbon Pellets, Sample C
(Space Velocity: 100,000 v/v/h)

Temperature, °C	Burn-Off Rate, %/h(1)
316	0.006
371	0.05

---

(1) Rate = $\frac{\text{Wt. loss} \times 100}{\text{Avg. wt.} \times \text{time}}$

The oxidation rate was high at 371°C (700°F) and may be unacceptable for long service life. The rate of carbon oxidation for a viable system should probably be less than 0.01%/h. No further laboratory work was carried out because of the high burn-off rate at the realistic vehicle operating temperature of 371°C.

III.3.9.2 Magnesium Hydroxide

A sample of magnesium hydroxide pellets, R-987, specially prepared by Merck and Company, showed lower $SO_4^=$ removal rate than the benchmark sorbent (Table III-25). In addition, $Mg(OH)_2$ pellets showed about 16% loss in weight, possibly due to exfoliation of $MgSO_4$ from the surface. The $SO_4^=$ trapping efficiency averaged 75% for the ten hour test, however SO_2 sorption was 30%. No further work was conducted with this material.

III.3.9.3 $Ca(OH)_2$ and Colloidal Silica

A single wet mixture of $Ca(OH)_2$ was made using Ludox colloidal silica. To a wet paste of $Ca(OH)_2$ with water was added sufficient Ludox HS 40 colloidal suspension to make up 15% by weight of SiO_2. The resulting mix was dried, granulated and pelleted in the usual manner. Physical properties and laboratory activity results are shown in Table III-18. Sulfate trapping efficiency was poor, and no further work was done with this approach.

III.4 Vehicle Durability Testing of $SO_4^=$ Trap Sorbents

In the work described in Section III.3, the aim was to identify at least two compositions which could be fabricated into strong and durable sorbents. These sorbents were to provide good $SO_4^=$ removal efficiency and have a minimum effect on back pressure through the trap. In the present section, tests of the most promising sorbents are described, in vehicle mounted traps for 15 000 km. The sorbent compositions used were the following:

- 85% CaO/10% SiO_2/5% Na_2O rings (12.7 mm O.D.)
- 85% CaO/10% SiO_2/5% Na_2O pellets (4.76 mm O.D.)
- 85% $Ca(OH)_2$/15% SiO_2 (Dicalite) pellets (4.76 mm O.D.)

III.4.1 Summary of Results

Three vehicle durability runs were made, using oxidation catalyst-equipped vehicles with trap canisters containing the $SO_4^=$ trap sorbent candidates. The benchmark material ($CaO/SiO_2/Na_2O$) was used in the form of rings and also pellets, and a sodium-free calcium sorbent ($Ca(OH)_2/SiO_2$) was evaluated in the form of pellets.

None of the durability tests were extended beyond 15 000 km because of the significant loss in $SO_4^=$ removal efficiency of the sorbents with kilometer accumulation. The sorbents showed above 90% $SO_4^=$ trapping, and also high SO_2 sorption at 0 km. As the test progressed, the SO_2 sorption decreased, but unfortunately, $SO_4^=$ removal also decreased, to

TABLE III-15

EVALUATION OF SORBENTS IN THE LABORATORY SCREENING TEST

Composition	Final Heat Treating Conditions	Density g/cm³	Crush Strength, lb Initial	Crush Strength, lb After Reactor Test	Laboratory Reactor Screening Test 100,000 r/hr, 150°C: Total Exposure To Fuel Gas, Hours	I_2^* Trapping Efficiency, %	I_2 Trapping Efficiency, %
Carbon (Calgon) Sample C	-	-	13.5	11.4	1.8	61	0
					4.8	76	5
					5.3	62	8
					6.3	75	11
					9.1	76	11
$Mg(OH)_2$ (Merck and Co., Inc.) Sample B-987	-	-	9.4	4.2	1.6	85	43
					2.3	79	32
					4.3	74	30
					5.7	76	28
					7.9	64	24
					9.9	66	24
CaO/SiO2/MgO (85/15/5) (RE 4738-26) (3.2 mm OD pellets)	35 hours @ 315°C	1.380	8.6	15.8	1.6	86	32
					2.6	89	33
					4.6	89	37
					6.8	90	38
					7.6	87	39
					9.6	87	39

below 90%. The benchmark pellets and the sodium-free sorbent showed essentially equivalent trapping efficiency after accumulating 15 000 km. These two preparations were more effective than the benchmark rings.

The back pressure through the $SO_4^=$ traps during the durability runs remained negligible. Physical inspection of the sorbents at the end of the test showed no deterioration and no build-up of fines in the trap. The fabricated sorbents were hard and strong and withstood vehicular testing.

III.4.2 Experimental Procedures

III.4.2.1 Vehicle Preparation

Vehicle tests were conducted using two cars with 351 CID V-8 engines; a 1973 and a 1974 model. Both vehicles were equipped by us with two Engelhard PTX-11B ® Pt-Pd monolith oxidation catalysts, one on each bank of the engine in the post-manifold position. The vehicles were also each equipped with an air pump. The traps consisted of the conventional 4.25 litre canisters normally used by General Motors for pellet oxidation catalysts. The traps containing the experimental sorbent particles were placed in the exhaust system under the rear seat, and the standard mufflers were removed to accommodate the $SO_4^=$ traps.

III.4.2.2 Test Fuel

All the kilometer accumulation and testing done in this program were conducted using a 0.032 wt % sulfur content gasoline. Several typical inspections on the test fuel are presented in Table III-26.

III.4.2.3 Test Procedure

All the kilometer accumulations were carried out on automatic mileage accumulation dynamometers using the modified AMA durability cycle. Periodically, the vehicles were emission tested using the Exxon Research exhaust particulate sampler described in Appendix C. Each sorbent was evaluated for 15 000 km on a vehicle including emission testing at the following points: 0, 5 000, and 15 000 kilometers. Initially, measurements were obtained at 0 km with and without the $SO_4^=$ trap installed. The test sequence used for each emission test was the following: FTP, HET, SET, FTP, SET, HET, and 96 km/h (2 hours). Measurements were made of total sulfates, as well as gaseous emissions of CO, HC, and NO_x. Also, pressure drops across the trap at idle and at 64 km/h cruise mode were obtained. The results for each of the durability runs are recorded in Appendix D, Tables D-1 through D-3.

TABLE III-26

TEST FUEL BLEND

RVP, kPa	88.6 (12.9 psi)

% Evap.	
T °C	% Off
40	5
55	20
98	50
171	90

Breakdown Time, minutes	960
Gravity, g/cc	0.7599
Sulfur, ppm	120
Lead, g/l	<0.002
FIA, Vol %	
Aromatic	25.1
Olefin	10.6
Saturates	64.3
Research Octane	93
Motor Octane	86

III.4.3 $CaO/SiO_2/Na_2O$ (Benchmark) Rings

In the two vehicle durability tests previously performed with 85% CaO/10% SiO_2/5% Na_2O sorbent, two particle geometries were employed. The first test used 3.2 mm cylindrical pellets. In the second test, cylindrical rings of 15.9 mm O.D., 5.6 mm I.D., and 7.9 mm height were used. Pressure drop across the trap bed was a major problem with the pellets, which, after 20 400 km, was 20 kPa at 64 km/h cruise. At similar kilometers, using the rings, the pressure drop was only 4.2 kPa. Although pressure drop with the rings was lower, $SO_4^=$ sorption efficiency was only 50% after 11 000 km compared to more than 95% for the pelleted material. These results are presented in detail in the Final Report for Phase 1 of this contract(1).

In considering another sorbent geometry, our targets were a better combination of low pressure drop and high $SO_4^=$ sorption efficiency, especially after extended operation. The pressure drop in a fixed bed can be decreased by increasing the void fraction in the bed, and also by increasing effective particle size. The sorption efficiency can be raised by increasing the total surface area of the rings in the trap bed. In Table III-27 are listed calculated void fractions and surface areas for several geometries of trap particles, assuming 0.35 as the void space for packed beds of right cylinders.

In the case of the rings previously used (geometry D, Table III-27), the void space was increased by 23%, relative to the 3.2 mm pellets. However, this was at the expense of the total surface area, which for the rings was only 34% that of the pellets. These effects probably account for the reduced pressure drop with the rings, and the loss in trapping efficiency. It was decided to fabricate rings of geometry E, using the benchmark sorbent, for vehicle testing, since the total surface area for E is greater than for rings D or F and the void fraction is also high.

III.4.3.1 Experimental Results

A Kilian T-5 single station tablet press was used to fabricate the rings from powder prepared as described in Reference (1), p. 48. Because of greater void volume and more surface area, the new geometry was expected to afford less pressure drop and greater $SO_4^=$ trapping efficiency in comparison to the rings previously tested. After heat treating at 315°C, the new rings had an average crush strength of 3.2 kg and a density of 1.263 g/cm³. Packing characteristics were determined using a graduated cylinder having an inside diameter of 14.4 cm. A 3.8 litre packed bed weighed 2.12 kg, corresponding to a void fraction of 0.56. This experimental void fraction is close to the predicted value of 0.51.

TABLE III-17

SURFACE AREA AND VOID SPACE IN PACKED BEDS OF PELLETS AND RINGS

	Cylindrical Pellets			Cylindrical Rings		
	A	B	C	D	E	F
Outside Diameter, mm	3.20	4.76	6.35	15.9	12.7	19.0
Inside Diameter, mm	—	—	—	5.6	6.4	9.5
Height, mm	3.2	4.76	6.35	7.9	6.4	6.4
Void Fraction in Packed Bed*(6)	0.35	0.35	0.35	0.43	0.51	0.51
Surface Area Per Particle, mm^{-1} / Volume per particle**	1.89	1.26	0.94	0.66	0.94	0.74
Total Surface Area, mm^{-1} / Total bed volume***	1.23	0.82	0.61	0.42	0.61	0.48

* Void Fraction = 0.35 + 0.65 $\left(\frac{ID}{OD}\right)^2$

The first term, 0.35, is the void space found for right cylinders, having height = outside diameter

** $\frac{\text{Surface Area per particle}}{\text{Volume per particle}} = \frac{2}{\text{Height}} + \frac{4}{(OD - ID)}$

*** $\frac{\text{Total Surface Area}}{\text{Total Bed Volume}} = 0.65 \left(\frac{\text{Surface Area per particle}}{\text{Volume per particle}}\right)$

A standard 4.26 litre GM oxidation catalyst reactor was charged with 2.21 kg of the benchmark rings. The trap was installed on a 1974 car, equipped with V-8 engine, air pump, and two PTX-11B® oxidation catalysts (the test vehicle described in Section III.4.2.1).

The results obtained with this vehicle are shown in Appendix B, Table B-1. Prior to installing the trap, $SO_4^=$ emissions were obtained. All testing and kilometer accumulation was done using the 320 ppm sulfur test fuel. The baseline emission tests at 0 km, with and without the $SO_4^=$ traps installed, showed that the $SO_4^=$ trapping efficiency for these rings was less than obtained with the rings previously tested (O.D. 15.9 mm). Since the new sorbent geometry provided greater geometric surface area, it was surprising that the sorption efficiency was less. However, the fabrication of stronger rings with controlled sodium content may have resulted in less efficient sorbent. Trapping efficiency at 0 km was 51.7% during the EPA Sulfate Emission Test cycle (SET). The back pressure through the trap was negligible under idle and 64 km/h cruise (Appendix D, Table D-4). The pressure drop through the trap was only 0.5 kPa.

It was decided to continue this test, since it was of interest to know how $SO_4^=$ trapping efficiency is maintained as a function of test kilometers. The test vehicle accumulated kilometers using the modified AMA durability cycle on the automatic mileage accumulation dynamometer. After accumulating 6 400 km, the $SO_4^=$ removal efficiency had significantly decreased to 26.7% under the SET. The back pressure through the trap continued low at 0.5 kPa at idle and 0.9 kPa at 64 km/h. The test vehicle accumulated an additional 10 000 km to obtain an additional check on the performance of the benchmark rings. The test car was evaluated at 16 000 km with and without the trap installed. The $SO_4^=$ trapping efficiency was higher and similar to that observed at 0 km under SET, but showed no $SO_4^=$ removal under the FTP testing mode. The $SO_4^=$ measurements with and without the trap on the vehicle at 16 000 km are summarized as follows:

Table III-28

1974 Vehicle (351 CID, PTX-11B)
$SO_4^=$ Emissions, SET Cycle @ 16 000 km

	$SO_4^=$, g/km
With trap installed	0.0051
Without trap	0.0105
% Efficiency*	51.4

$$* \quad SO_4^= \text{ trapping efficiency} = \left(1 - \frac{SO_4^= \text{ with trap @ 16 000 km}}{SO_4^= \text{ without trap @ 16 000 km}}\right)$$

The pressure drop through the trap remained low; 0.5 kPa idle and 1.0 kPa at 64 km/h. The 16 000 km results showed that the 12.7 mm O.D. rings provided better trapping durability than the rings (15.9 mm O.D.) previously tested. The new sorbent provided a better geometric surface and harder rings. However, the rings were not as efficient as the previously tested benchmark pellets, and the vehicle testing was terminated after reviewing the results with the EPA.

III.4.4 $CaO/SiO_2/Na_2O$ (Benchmark) Pellets

A large batch of $CaO/SiO_2/Na_2O$ (85/10/5) was prepared and fabricated into 4.76 mm O.D. pellets for vehicular evaluation. The powder was different than the original benchmark material described in Reference 1, being prepared with better control of Na_2O content, and with improved crush strength, using the techniques described in Sections III.3.2.1 and III.3.4.1. It was our intention that these pellets would provide better control of back pressure than did the originally tested 3.2 mm pellets; in addition, they should provide better $SO_4^=$ sorption than did the cylindrical rings of 12.7 mm O.D. Also, the 4.76 mm pellets have a higher surface area to volume ratio, 1.26 mm^{-1}, versus 0.94 mm^{-1} for the rings (Table III-27).

III.4.4.1 Experimental Results

A standard 4.26 litre GM oxidation catalyst canister was charged with the benchmark pellets. The trap was installed on a 1974 car, equipped with a V-8 engine, air pump, and two PTX-11B® oxidation catalysts. The vehicle was set to manufacturer's specifications, and no attempt was made to meet any particular emission standards. The NO_x emission levels are higher than the standards and was possibly due to a malfunctioning EGR valve. The results obtained with the vehicle equipped with the 4.76 mm benchmark pellets are reported in Appendix D, Table D-3.

Prior to kilometer accumulation, emission levels were measured at 0 km, with and without the trap installed. The $SO_4^=$ trapping efficiency under the SET, FET, and 96 km/h testing modes was greater than 95%, while under FTP conditions, only 36%. For example, under the SET testing mode, the average $SO_4^=$ emission was 8.8 mg/km without the trap and 0.4 mg/km with the benchmark sorbent in the trap. Similarly, under 96 km/h cruise, $SO_4^=$ level was 25.9 mg/km without the trap and 0.4 mg/km with the trap. The back pressure through the trap was negligible. After 5 000 km, the cyclic $SO_4^=$ sorption efficiency had fallen slightly.

The test vehicle accumulated an additional 10 000 km, and it was again tested under the different testing modes. In addition, baseline emissions were obtained on the vehicle with the $SO_4^=$ trap removed. At 15 000 km, the results showed a significant decrease in the sorbent's efficiency. In Table III-28, the $SO_4^=$ emission levels and trapping efficiencies are summarized.

TABLE III-29

VEHICULAR DURABILITY TESTING OF $SO_4^=$ SORBENT TRAPS

$CaO/SiO_2/Na_2O$ Pellets (4.76 mm O.D.)

	$SO_4^=$ Emissions, mg/km				
	No Trap		With Trap		
	0 km	13 000 km	0 km	5 000 km	13 000 km
FTP	4.1	3.0	2.7	2.9	4.1
SET	8.8	2.1	0.4	0.8	1.8
FET	10.6	5.6	0.3	0.8	1.5
96 km/h	25.9	18.7	0.4	0.5	3.0

	$SO_4^=$ Trapping Efficiency, %			
	0 km*	5 000 km*	13 000 km*	13 000 km**
FTP	34	29.0	0	0
SET	95.5	90.9	79.5	14.3
FET	97.2	92.5	85.8	73.2
96 km/h	98.5	98.1	88.4	83.9

* $SO_4^=$ trapping efficiency = $\left(1 - \frac{SO_4^= \text{ with trap}}{SO_4^= \text{ with trap @ 0 km}}\right)$

** $SO_4^=$ trapping efficiency = $\left(1 - \frac{SO_4^= \text{ with trap}}{SO_4^= \text{ with trap @ 13 000 km}}\right)$

The $SO_4^=$ emission levels without the trap installed showed a decrease at 15 000 km from those obtained at 0 km, indicating some loss in catalyst activity during the evaluation period. However, the $SO_4^=$ emission results reconfirm that the $CaO/SiO_2/Na_2O$ pellets showed a significant loss in $SO_4^=$ removal efficiency.

During the 15 000 km test, the back pressure through the trap was negligible (Appendix D, Table D-4), and inspection of the pellets and the trap at the end of the test showed no accumulation of fines. This suggests that the pellets had improved crush strength, compared to those described in Reference 1. However, because of increased hardness, the $SO_4^=$ trapping, as measured under the different testing modes, was poorer than observed with the originally tested benchmark pellets. After reviewing the results with the EPA, it was agreed that no further testing of the benchmark sorbent was warranted.

III.4.5 $Ca(OH)_2/SiO_2$ (Dicalite) Pellets

A large batch of $Ca(OH)_2/SiO_2$ (Dicalite) (85/15) pellets was prepared using the wet mixture preparation described in Section and fabricated into 4.76 mm O.D. pellets. This is a sodium free preparation, which is intended to minimize sorbent pick-up of SO_2.

III.4.5.1 Experimental Results

A GM oxidation catalyst canister was charged with the pellets and installed on a 1973 V-8 car, equipped with an air pump and two PTX-IIB catalysts in the post manifold position. The detailed emission results obtained during the 15 000 km durability test are reported in Appendix D, Table D. A summary of the $SO_4^=$ emissions and trapping efficiencies is presented in Table III-30.

Sulfate emission levels were measured at 0 km, with and without the $SO_4^=$ trap installed. The $SO_4^=$ emission levels without the trap were higher than $SO_4^=$ levels observed with the 1974 car used to evaluate the benchmark sorbent. The differences in $SO_4^=$ activity between the two catalyst pairs is partially due to differences in catalyst activity. The PTX-IIB on the 1973 car had accumulated approximately 20 000 km, while the PTX-IIB on the 1974 car had been aged for 50 000 km.

The $SO_4^=$ removal at 0 km was equivalent to the benchmark sorbent, but then decreased significantly. The $SO_4^=$ removal from 5 000 km to the end of the test remained at about the same level, with 50-60% $SO_4^=$ removal under the testing modes, except FTP, where trapping was ineffective. In fact, the operating conditions of the car apparently changed, so that the $SO_4^=$ production over the catalysts during the FTP, and hence $SO_4^=$ emissions, increased from the 0 km no trap test. This made a quantitative measure of trap efficiency at 5 000 and 15 000 km impossible for the FTP. However, the significant decrease in activity during the other test modes confirmed the decision to cease testing this sorbent.

TABLE III-30

VEHICULAR DURABILITY TESTING OF $SO_4^=$ SORBENT TRAPS

$Ca(OH)_2$/Dicalite (4.76 mm O.D.)

	$SO_4^=$ Emissions, mg/km			
	No Trap	With Trap		
	0 km	0 km	5 000 km	15 000 km
FTP	4.5	1.5	10.8	12.7
SET (4 tests)	38.4	1.1	16.4	16.0
FET	35.4	0.8	12.3	13.4
96 km/h (2 hours)	51.7	5.7	20.6	19.4

	$SO_4^=$ Trapping Efficiency, %*		
	0 km	5 000 km	15 000 km
FTP	66.6	----	----
SET (4 tests)	96.4	57.3	58.4
FET	97.7	65.3	62.1
96 km/h (2 hours)	89.0	60.2	62.5

* $SO_4^=$ trapping efficiency = $\left(1 - \frac{SO_4^= \text{ with trap}}{SO_4^= \text{ without trap @ 0 km}}\right)$

The back pressure through the trap at idle was 0 kPa, and at 64 km/h, 0.75 kPa. Physical inspection of the pellets showed no visible deterioration. The sodium free sorbent formed hard pellets and withstood vehicular testing. Unfortunately, the sorbent was not effective. The removal of sodium from the sorbent composition adversely affected its sulfate pick-up properties.

III.4.6 Conclusions from Vehicle Durability Evaluation

None of these durability tests were extended beyond 15 000 km because of the significant loss in $SO_4^=$ removal efficiency of the sorbents. Both the pellet sorbents showed about 90% or better $SO_4^=$ removal at 0 km for the SET, but the sorbents also showed high SO_2 removal. As the tests progressed, SO_2 removal dropped rapidly. The benchmark pellets and the sodium free pellets showed overall better $SO_4^=$ trapping than the benchmark rings, probably due to differences in the total surface area of the pellets versus the ring geometry. The three sorbents at 15 000 km were not effective in removing $SO_4^=$ under the FTP testing mode, but showed significant differences under the other testing modes.

The back pressure through the $SO_4^=$ traps was negligible during the three durability tests. Physical inspection of the rings and pellets at 15 000 km showed no visible deterioration and no build-up of fines in the trap. The fabricated sorbents formed strong and hard rings and pellets which withstood vehicular testing. Unfortunately, these stronger and harder sorbents were not effective on extended testing.

IV. Modification II - Effect of Noble Metal Composition on Catalyst Activity

IV.1 Summary of Results

Three pairs of monolith oxidation catalysts were prepared by Matthey-Bishop, Inc., differing primarily in noble metal composition. The noble metal compositions were Pt-Pd, Pt-Rh, and Pt. These catalysts were evaluated sequentially on the same car for 12 800 km each. The Pt-Rh catalyst was found to give the lowest sulfate emissions under every testing mode. The Pt-Pd and Pt catalysts gave higher sulfate emissions and were roughly comparable to each other. For example, the average sulfate emission levels measured using the EPA Sulfate Emission Test were the following, with the test fuel containing 320 ppm sulfur.

Catalyst	Average $SO_4^=$, g/km
Pt-Rh	0.010
Pt-Pd	0.025
Pt	0.030

During the program, the other gaseous emissions were similar for all three catalysts at these low mileages.

The results confirm a growing body of data that Pt-Rh containing catalysts are lower sulfate emitters than other commercial catalysts, and the noble metal composition itself, in addition to or instead of other factors, such as support type, is playing a major role. The data offer strong support for the possibility of developing selective catalysts which have high activity for CO and HC oxidation and low activity for SO_2 oxidation.

IV.2 Introduction

This program, Modification II, is an extension to Contract No. 68-03-0497, "An Assessment of Sulfate Emission Control Technology". The purpose of this work is to help determine whether or not noble metal composition changes are the major factors causing the observed differences in sulfate emissions from various commercial catalysts.

Since the oxidation of SO_2 in automotive exhaust is a catalytic process, it is to be expected that different catalysts will show different emission rates. One of the most promising approaches to $SO_4^=$ control is the use of catalysts which are selectively more active for CO and HC oxidation than they are for SO_2 oxidation. Beltzer, et al.,(2) reported that Pt-Rh monoliths showed significantly less SO_2 oxidation than nominally similar Pt-Pd monoliths. This finding was subsequently verified by Bradow and Moran(5). Some of the data obtained by Holt, et al.,(7) indicated that Pt catalysts might have higher $SO_4^=$ emission rates than Pt-Pd catalysts. In a recently completed API sponsored program(8), similar trends among catalyst systems on $SO_4^=$ emissions were observed.

The above studies were confounded by the fact that many other catalyst properties, besides noble metal composition, were different. Thus, catalysts from different manufacturers were used, and it is probable that, in addition to noble metal composition, such parameters as the amount and composition of washcoat, surface area, and pore volume, noble metal loading, and cell geometry, varied between catalysts. To reduce ambiguity in this program, one manufacturer, Matthey-Bishop, Inc., prepared the three catalyst pairs, holding all other properties, except noble metal composition, constant as far as possible.

The program was originally divided into two tasks. Task 1 involved the testing of three fresh catalysts, identical in all respects as far as possible, except for their noble metal composition. Task 2 required the testing of two aged catalysts (40 000 km), which were also as similar as possible, except for noble metal composition. However, the latter pair of catalysts did not become available, as had been expected, so this part of the program was not done.

The results from Task 1 evaluated whether the noble metal composition changes are the major factors affecting the observed differences in $SO_4^=$ emissions. Task 2 would have provided data on whether such differences are maintained over the useful life of the catalysts.

IV.3 Experimental

IV.3.1 Monolith Oxidation Catalysts

Three pairs of monolithic oxidation catalysts were prepared by Matthey-Bishop, Inc. for use in this program. They were as identical as possible, except for their noble metal composition, which consisted of Pt, Pt-Pd, and Pt-Rh. A description and characterization of the catalysts are summarized in Table IV-1. The catalysts supplied by Matthey-Bishop were made from Corning ceramic monoliths, extruded honeycomb structures containing approximately 31 channels per cm^2 of cross sectional area. The catalysts contained an alumina washcoat and a noble metal loading of approximately 1.6×10^{-3} g/cm^3. The Pt catalyst's H.S.A. coating surface area was about 2 times higher than the other two prepared catalysts, but the washcoat loading for all three catalyst pairs was equivalent.

TABLE IV-1

CATALYST CHARACTERIZATION*

	Pt-Pd** [illegible]		Pt-Rh [illegible]	Pt [illegible]
	I	II		
B.S.A. Coating Surface Area (m^2/cm^3)	22.1	20.2	18.7	22.5
Catalyst Loading (g/cm^3)	1.8×10^{-3}	1.6×10^{-3}	1.6×10^{-3}	1.5×10^{-3}
Catalyst Surface Area (m^2/cm^3)	0.12	[illegible]	0.26	0.11
Washcoat Loading (g/cm^3)	0.10	0.10	0.11	0.12
Substrate	32 cell/cm^2			
Size	12.5 cm diameter x 7.5 cm length			

* Characterization provided by Matthey-Bishop, Inc.

** An additional pair of Pt-Pd catalysts was prepared because one of the catalysts failed during mileage accumulation.

IV.3.2 Test Vehicle

The monolith catalysts were evaluated on a 1975 Ford LTD with a 5.85 litre V-8 engine. The car was equipped with an air pump. This vehicle exhaust system had been modified to accept two monolith catalysts in the post manifold position. The test vehicle had been used previously in Contract No. 68-03-0497 and described in the previous final report of Phase I, Section V.2.1[1]. Before starting the emission test sequence with each set of catalysts, the vehicle was tuned-up and set to manufacturer's specifications.

IV.3.3 Test Fuel

The test fuel contained 0.032 wt % sulfur. The fuel was blended from a base fuel by the addition of equal amounts of thiophene and di-t-butyl disulfide. Typical inspections on the test fuel are summarized in Table IV-2.

IV.3.4 Test Sequence

The catalyst pairs were tested sequentially on the same vehicle using the same test equipment in order to maintain uniformity in aging and test conditions. $SO_4^=$ and other gaseous emissions were measured using the following sequence:

1975 Federal Test Procedure (FTP)
Federal Economy Test (FET)
EPA Sulfate Emission Test (SET)
Idle (20 minutes)
64 km/h one hour cruise
96 km/h one hour cruise

After the initial emission test sequence, the test vehicle was placed on the automatic mileage accumulation dynamometer (MAD), and accumulation was carried out using the ERE turnpike cycle having an average speed of 91 km/h. At intervals of 3 200, 6 400, 9 600, and 12 800 km, the vehicle was put through the above emission testing sequence. The preconditioning between FTP tests was 3 200 km of MAD accumulation, while the preconditioning for the other portions of the test sequence was the preceding $SO_4^=$ emission test.

Standard instrumentation was used for CO, HC, and NO_x measurements. $SO_4^=$ emissions were measured using ERE's CVS exhaust particulate sampler[8] and SO_2 emissions were measured using an H_2O_2 bubbler technique. Measurements for $SO_4^=$ were made for the entire FTP, FET, SET, and idle tests, but were broken into half hour segments for the two cruise modes. A more detailed description can be found in the final report on Phase I of Contract No. 68-03-0497, Section IV.1.3[1].

TABLE IV-2

TEST FUEL BLEND

RVP, kPa	68.8 (10.0 psi)
% Evap. @ °C	
45	5
64	20
112	50
179	90
Breakdown time, minutes	960^{+}
Gravity, g/cc	0.7596
Sulfur, ppm	320
Lead, g/l	<0.002
FIA, Vol. %	
Aromatic	35.5
Olefin	6.9
Saturates	56.6

IV.4 Results

This program provided data on the effect of noble metal composition changes on automotive sulfate emissions, at least with relatively fresh systems. The total kilometer accumulation was too short to see any appreciable effect of catalyst aging.

The test sequence run with the Pt-Pd catalysts was repeated with a new pair of Pt-Pd catalysts because inspection of the catalysts at the end of the first 12 800 km test showed that one catalyst had partially melted. The catalyst's failure was probably due to an overtemperature while accumulating kilometers on the automatic mileage accumulation dynamometer. As the test progressed, an increase in CO and HC emissions were observed. Initially, we thought the increase in emissions was caused by a malfunctioning carburetor, however, the partial loss of one converter would account for the increase. The catalyst failure was probably due to ignition system failure. Apparently, the dump value which is operated by a thermal switch was not able to protect the catalysts from overtemperature. A new ignition system was installed in the test vehicle before installing the next pair of catalysts.

The individual $SO_4^=$ emissions and other gaseous emissions on each catalyst pair are included in Appendix E (Tables E-1 to E-3). The fuel consumption and exhaust temperatures are reported in Appendices F and G, respectively. All the data on the initial runs on the Pt-Pd catalyst that burned up are reported in Appendix H.

IV.4.1 Sulfate Emissions

Analysis of the $SO_4^=$ test results on the three pairs of oxidation catalysts showed that the Pt-Rh catalysts provided the lowest $SO_4^=$ emission levels at each test interval and under each testing mode. These results are graphically illustrated in Figures IV-1 to IV-5. It is interesting to note that at 0 km, the Pt catalysts showed lower $SO_4^=$ levels than the Pt-Pd, but as the test progressed, the Pt catalyst directionally showed higher $SO_4^=$ levels. This low mileage behavior of the Pt catalyst may have been caused by its higher washcoat surface area, which could provide greater initial storage capacity for $SO_4^=$. No attempt was made at drawing the best line through all the data points, since each data point is one test/mode/test interval. In general, $SO_4^=$ emission levels were the highest using the steady state cruise testing modes. The $SO_4^=$ emissions at 0 and 12 800 km under each testing mode are summarized in Table IV-3. Individual $SO_4^=$ emission results at each test interval are reported in Appendix E.

IV.4.2 Other Gaseous Emissions

All three catalysts gave similar CO and HC emission levels during the 12 800 km test. Individual gaseous emission results are

TABLE IV-3

SULFATE EMISSIONS AT START AND FINISH OF MILEAGE ACCUMULATION

Test Sequence		$SO_4^{=}$ Emissions, g/km					
		0 km			22 400 km		
		Pt-Rh	Pt-Pd	Pt	Pt-Rh	Pt-Pd	Pt
FTP		0.004	0.009	0.006	0.007	0.014	0.021
FET		0.005	0.034	0.009	0.020	0.055	0.064
SET		0.004	0.028	0.010	0.009	0.026	0.031
Idle (20 min.)*		- - -	0.003	0.019	0.017	0.018	0.018
64 km/h (1 hr)**	I	0.008	0.064	0.016	0.024	0.062	0.058
	II	0.011	0.057	0.043	0.023	0.059	0.055
96 km/h (1 hr)**	I	0.025	0.063	0.036	0.028	0.062	0.065
	II	0.027	0.053	0.031	0.022	0.052	0.047

---

* $SO_4^{=}$ results at idle reported as g/hour.

** The two cruise modes were broken up into two half-hour segments.

FIGURE IV-1

$SO_4^=$ EMISSIONS - 1975 FTP

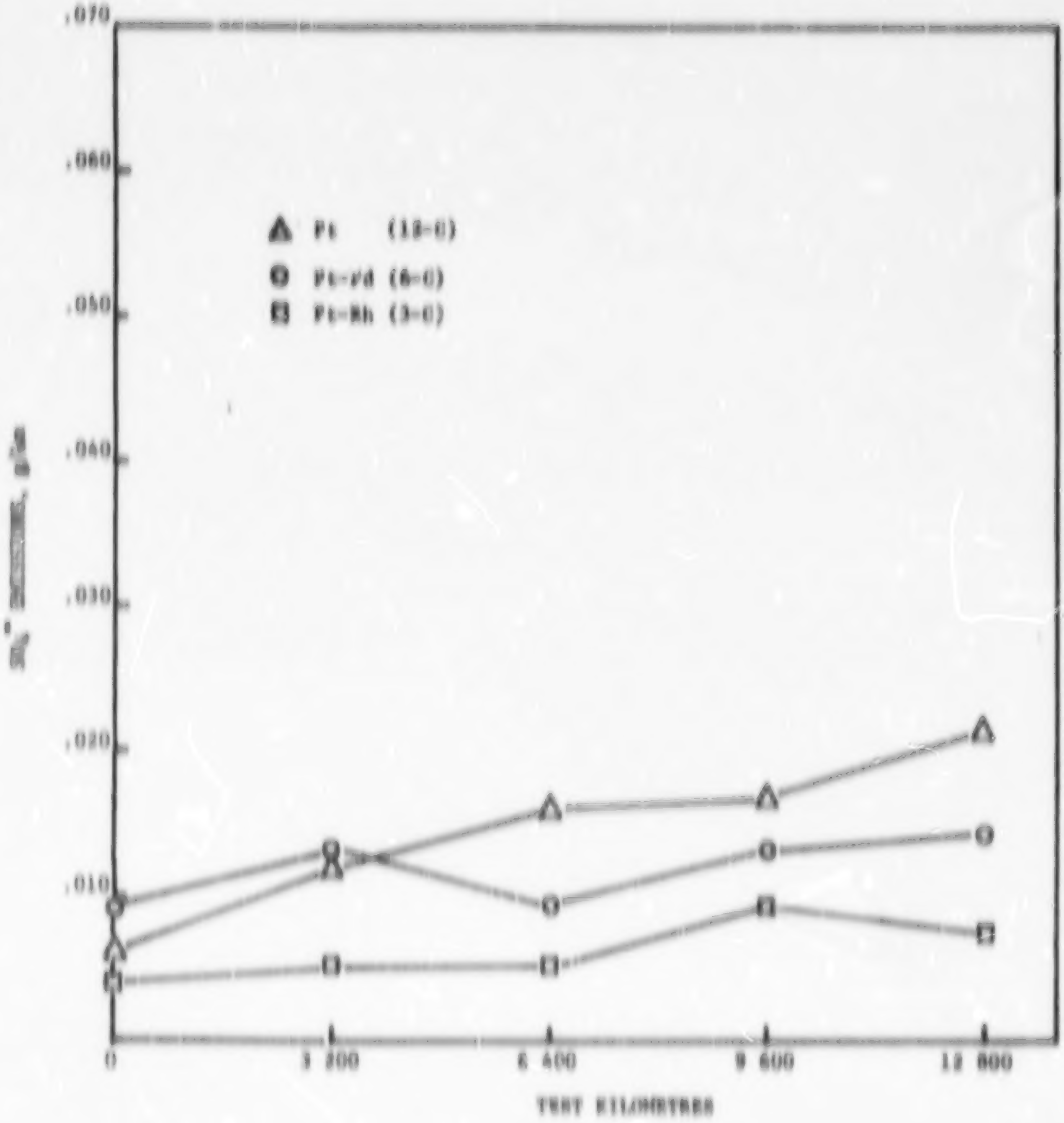


FIGURE IV-2

$SO_4^=$ EMISSIONS - FTP CYCLE

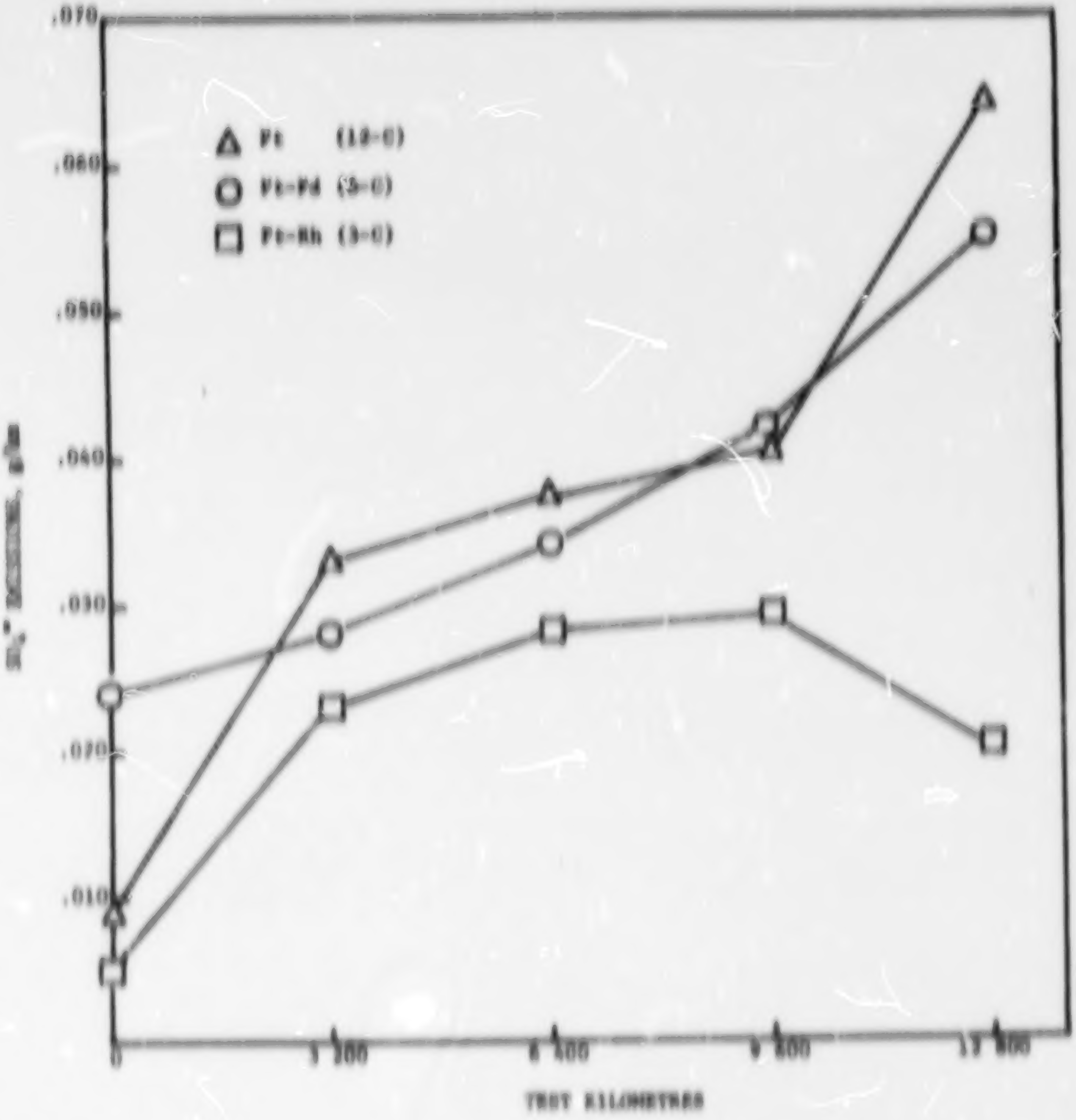


FIGURE IV-3

$SO_4^=$ EMISSIONS - SET CYCLE

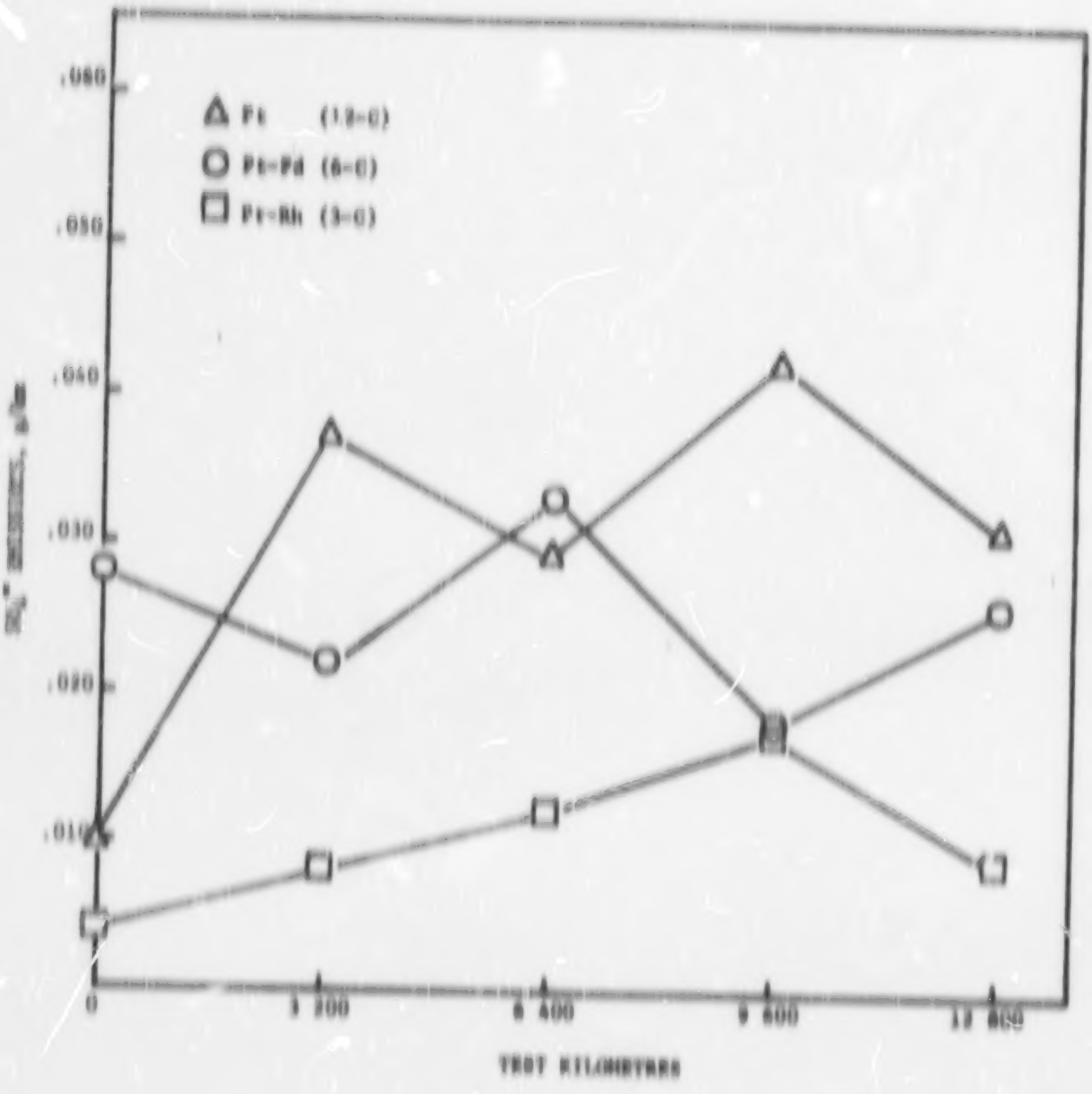


FIGURE IV-4

$SO_4^=$ EMISSIONS - 64 km/h CRUISE

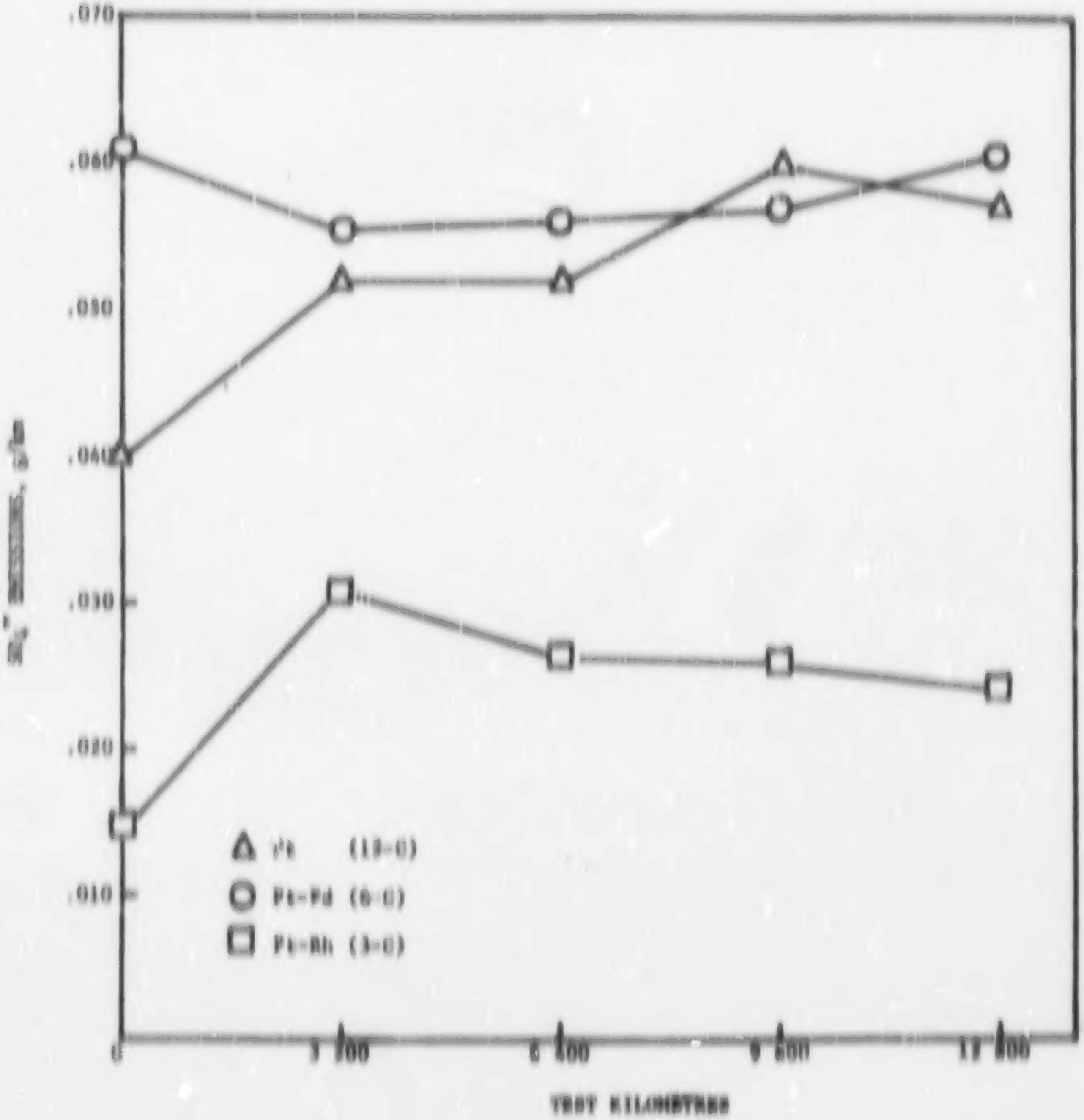
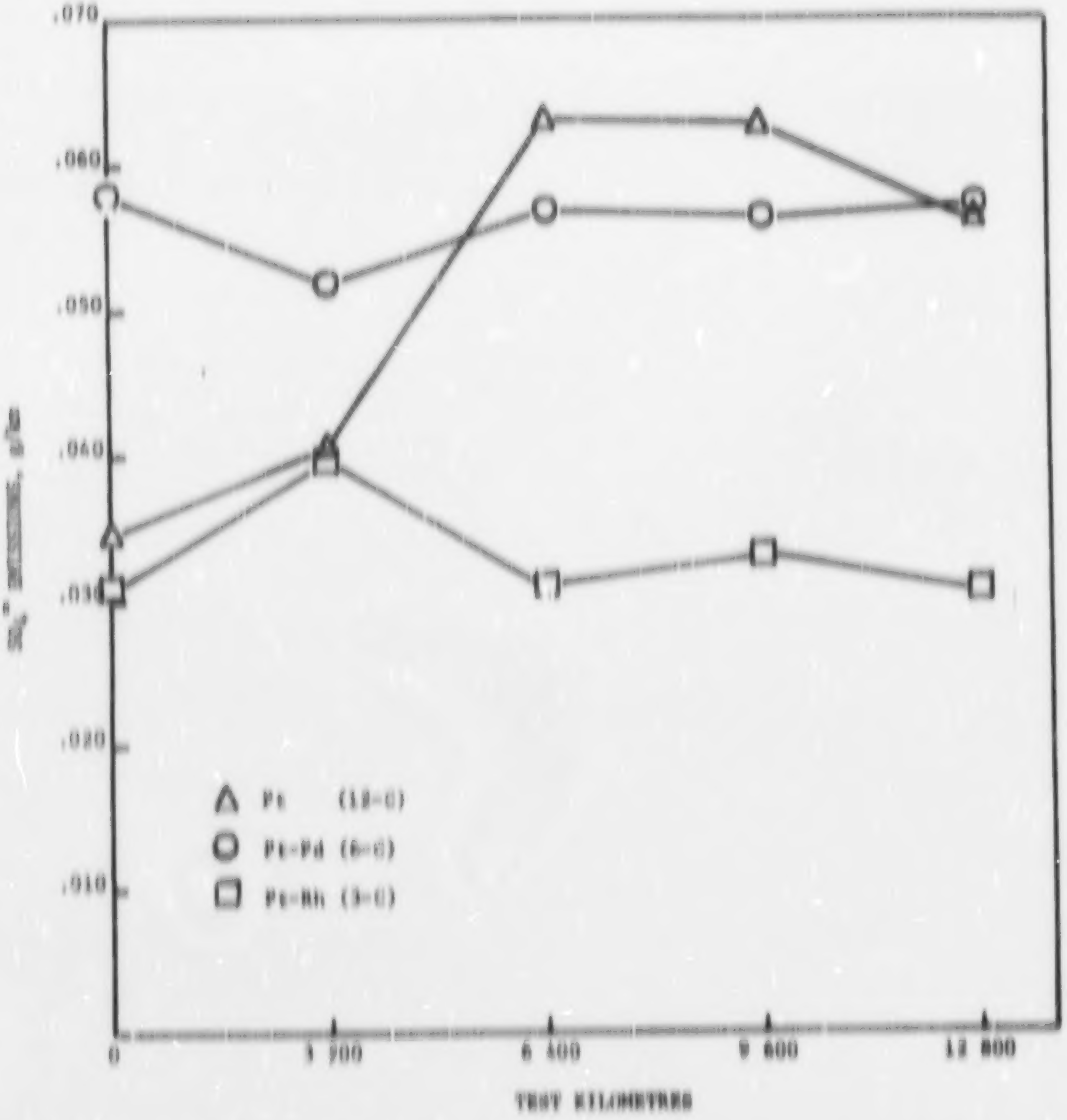


FIGURE IV-5

$SO_4^=$ EMISSIONS - 96 km/h CRUISE



tabulated in Appendix E. A summary of the average gaseous emissions measured during the program under FTP, FET, and SET testing modes follows (Table IV-4):

Table IV-4

Average Gaseous Emissions*

Catalyst	FTP, g/km			FET, g/km			SET, g/km		
	CO	HC	NO_x	CO	HC	NO_x	CO	HC	NO_x
Pt-Pd	2.77	0.43	1.69	0.21	0.10	2.41	0.67	0.10	2.24
Pt-Rh	3.27	0.37	1.68	0.23	0.05	2.73	1.18	0.05	2.50
Pt	2.28	0.33	1.78	0.52	0.08	2.58	0.09	0.10	2.43

* The gaseous emissions averaged over the 12 800 km test period.

The Pt-Rh catalyst pair gave higher CO emissions under the FTP and SET modes, but was low on the FET. Its HC emissions were low over all three test modes. The Pt catalyst pair was lowest in CO for the FTP and SET, but highest for the FET. HC emissions were roughly comparable to the other catalysts for all test modes. No explanation for this sometimes contradictory results are available.

IV.4.3 Fuel Consumption and Catalyst Outlet Exhaust Temperatures

The fuel consumption and catalyst outlet exhaust gas temperatures on each test run are tabulated in Appendices F and G. The fuel consumption was determined in two ways: the direct fuel weight and calculated from the emission data using the carbon balance method. The agreement in fuel consumption by the two methods was good. The fuel consumption for each testing mode remained relatively constant with minor fluctuations between runs for each catalyst system evaluated. Differences between catalysts are probably due to the fact that the test car was tuned-up each time catalysts were changed, resulting in slight variations in engine calibrations. A summary of calculated fuel economy under the SET modes follows:

Table IV-5

Fuel Consumption, g/km

	SET	Standard Deviation	Coefficient of Variation, %
Pt-Pd	118.6	6.2	5.2
Pt-Rh	121.7	5.8	4.8
Pt	126.2	2.7	2.1

Thermocouples were placed in the exhaust system at the outlet of the catalysts to measure exhaust gas temperatures. Some variation between catalyst pairs was observed, but as in the case of fuel consumption results, was probably due to slight changes in engine calibrations following tune-ups. Examples of the exhaust gas temperature ranges observed under the SET follow:

Table IV-6

Maximum Exhaust Gas Temperatures, °C
SET Cycle

Kilometers	Pt-Pd	Pt-Rh	Pt
0	607	671	654
3 200	613	671	582
6 400	571	671	616
9 600	577	616	517
12 800	604	649	616

IV.4.4 Oxygen Level in Exhaust Gas

The oxygen concentration in the raw exhaust ranged from 3.0-3.5% under the different testing modes. In this program, the air pump on the test vehicle was used at all times, so the three catalyst pairs were exposed to the same O_2 levels during $SO_4^=$ emission testing. Under each testing mode, excess O_2 was present in the exhaust gases.

IV.4.5 Conclusions

The Pt-Rh catalyst gave the lowest sulfate emissions under every testing mode at every test interval. The Pt-Pd and Pt catalysts gave higher $SO_4^=$ emissions and were comparable to each other. With the testing sequence used, sulfate emissions were highest under the steady state cruise conditions.

The results indicated that the noble metal composition is playing a major role in determining the rate of oxidation of SO_2 to SO_3. The program did not provide any data on whether the observed differences among catalysts on $SO_4^=$ emissions are maintained over the useful life of the catalysts. The data, however, offer strong support for the possible development of selective catalysts which have high activity for CO and HC oxidation and low activity for SO_2 oxidation.

V. Modification III - Perovskite Catalysts

V.1 Summary of Results

In both standard and high temperature vehicle configurations a pelletized perovskite catalyst showed poorer gaseous emission control than the GM pelletized catalyst. Sulfate emissions were also substantially higher for the perovskite catalyst in both vehicle configurations.

In tests with the vehicle in the high temperature configuration, it was found that a monolithic perovskite catalyst also exhibited poorer gaseous emission control than an Engelhard monolithic system. However, sulfate emissions from the perovskite monolith were lower than from the Engelhard monolith.

V.2 Introduction

This program was designed to evaluate the durability, activity, and sulfate formation activity of DuPont's perovskite Pt oxidation catalysts when used with unleaded fuel. According to DuPont, these catalysts possess a high degree of thermal stability. This stability presumably allows the catalyst to be operated at temperatures of about 700°C, with the vehicle using a leaded fuel, without incurring losses in catalyst activity due to poisoning by lead.

At the time this program was initiated, DuPont had begun vehicle testing with leaded fuel. However, they had not completed their program to optimize vehicle operating conditions for achieving the necessary high catalyst temperatures without incurring fuel economy penalties. Consequently, this program was restricted to testing DuPont's catalyst system in an unleaded environment at temperatures which would not entail a fuel debit. The objective was to provide information on the activity and durability of DuPont's catalysts in this type of environment, and thereby obtain a baseline case against which the effects of lead on activity and durability could be eventually assessed.

V.3 Experimental Conditions

Emission measurements were made using the following test sequence:

1975 FTP
2 SET
HFT
7 SET
64 km/h cruise (1 hour)

The test vehicle was a 1976 Ford LTD equipped with a 6550 cc engine and an air pump. Ford Motor Company provided cylinder heads with port liners to fit this engine. The DuPont catalyst pellets were packed into a standard GM catalyst canister. The size of the canister, 4.25 litres, precluded close placement of the catalytic reactor in the post manifold position. Each catalyst, when used, was placed in the underfloor position. The standard vehicle catalysts, of course, were removed. The sulfur content of both fuels, the unleaded kilometer accumulation fuel, and the unleaded indolene used for emission testing, was 300 ppm.

Kilometer accumulation was carried out on an automatic kilometer accumulation dynamometer using the modified AMA durability driving schedule. The modified AMA consisted of 11 laps, no wide open throttle accelerations, and 89 kph maximum speed.

Prior to initial emission testing, 1 050 km were accumulated on the test vehicle in consumer service to provide engine break-in and some combustion chamber deposits.

V.4 Emission Results

V.4.1 Vehicle Engine-Out Emissions

The vehicle was run through an FTP with the catalyst removed before initiating the kilometer accumulation. This procedure was repeated part-way through the test program. These steps were taken to provide a check on vehicle calibrations, to insure that major changes in carburetion or spark timing, which could significantly affect vehicle emissions, had not occurred. The FTP emissions, shown in Table V-1, indicate that the only significant change was a reduction in engine-out CO emissions.

Table V-1

Test Vehicle FTP Emissions Without Catalyst

	g/km			Fuel Economy
Vehicle km	CO	HC	NO_x	(km/l)
1 230	20.6	2.1	2.3	4.92
14 780	12.6	2.0	2.6	5.07

V.4.2 Emission Results with GM Pelletized Oxidation Catalyst

Table V-2 shows the emission results, starting with the fresh GM catalyst, up to the point where the catalyst had accumulated 13 300 km on the AMA driving cycle. The data for the four SET's has been averaged for each test sequence, as little variation in emissions was found over the four SET's in each test sequence. The 64 km/h cruise data represents the average of two bag samples and filters taken for two twenty minute sampling periods.

Gaseous emission values over the FTP are lower for the test sequence run after 6 640 catalyst km than initial measurements. This may have been due, at least in part, to a small leak that was discovered in the diaphragm of the sampling pump in the CVS system after the test sequence. The leak was repaired at this point. Sulfate measurements are unaffected by this leak. The 13 300 km results show the expected upward trend in HC emissions over the FTP and SET cycles, compared to the fresh catalyst values. The HET comparison is obscured by an abnormally high value in the fresh catalyst value. CO emissions are down at 13 300 km, but this is probably due to the lower engine-out emissions shown in Table V-1.

The rise in sulfate emissions by 6 640 km is in line with previous results obtained at Exxon in a study involving a twenty car fleet test[31], which showed that sulfate emissions peaked in this region. In the present test, the car was not run for a sufficient number of kilometers to begin showing the expected downward drift in sulfate emissions.

V.4.3 Emission Results with Pelleted DuPont Perovskite Catalyst

The perovskite catalyst tested contained 0.066 wt % Pt, or approximately 1.8 g Pt per 4.25 litre GM reactor. This is comparable to the loading of the GM pelletized oxidation catalyst, which is 0.055 wt % noble metal or 1.5 g Pt-Pd per reactor. Full emission test sequences were run after 3 300 km and 6 700 km. A duplicate FTP was performed at 3 300 km to confirm the gaseous emission results. The results of these test sequences are shown in Table V-3.

V.4.4 Comparison of Perovskite and GM Pelleted Catalysts at Normal Operating Temperatures

The perovskite catalyst showed poorer control of HC and CO emissions than the GM pelletized catalyst. The CO and HC emissions averaged over the kilometer accumulation for each catalyst are shown in Table V-4. The data in Table V-4 are the averages of 3 FTP's for each catalyst system. CO and HC emissions are higher for the perovskite catalyst by factors of 2.2 and 1.6, respectively. Overall conversions are also shown. These have been calculated by averaging the emissions from the two FTP runs made without the catalyst, which were shown in Table V-1.

TABLE V-2

EMISSION CHARACTERISTICS, VEHICLE EQUIPPED WITH OX CATALYST IN STOCK CONFIGURATION

Vehicle km	OX Catalyst km	Test	Emission Rates of Indicated Exhaust Components Gaseous Emissions, g/km CO	HC	NO_x	H_2SO_4 ** mg/km	Fuel Economy km/l
1 270	NONE	FTP	3.4	0.21	2.2	3.4 (2.6)	4.87
		SET*	4.6	0.20	1.8	1.1 (1.2)	6.76
		HFET	4.3	0.52	1.5	1.5 (1.8)	7.69
		64 km/h Cruise	0.04	0.08	1.3	1.0 (1.4)	9.25
7 925	6 640	FTP	2.4	0.20	1.7	9.4 (7.0)	4.79
		SET*	3.5	0.17	1.7	3.0 (3.2)	6.63
		HFET	1.2	0.10	1.6	7.0 (8.3)	7.50
		64 km/h Cruise	0.06	0.03	1.0	4.8 (9.2)	8.72
24 560	22 300	FTP	2.8	0.13	2.2	6.7 (4.9)	4.69
		SET*	1.2	0.25	2.0	5.6 (5.8)	6.64
		HFET	0.9	0.25	2.0	5.6 (5.8)	6.64
		64 km/h Cruise	0.03	0.14	1.3	8.4 (10.6)	8.55

---

* Average of 4 tests.

** Bracketed numbers are % conversion of fuel sulfur to sulfate, based on measured sulfate.

TABLE V-3

EMISSION CHARACTERISTICS, VEHICLE EQUIPPED WITH PELLETIZED DuPONT CATALYST IN STOCK CONFIGURATION*

Vehicle km	DuPont Catalyst km	Test	Emission Rates of Indicated Exhaust Components				Fuel Economy km/L
			Gaseous Emissions, g/km			H_2SO_4 ** mg/km	
			CO	HC	NOx		
19 120	3 330	FTP	6.1	0.41	2.3	3.5 (6.2)	4.71
		SET*	4.5	0.48	2.3	11.9 (12.6)	6.73
		HET	0.3	0.24	1.8	12.8 (15.5)	7.74
		64 km/h Cruise	0.04	0.12	1.5	13.2 (18.8)	9.03
19 310	3 540	FTP#	10.4	0.40	2.5	- - - - - - -	4.71
21 510	6 730	FTP	5.6	0.42	2.7	6.6 (4.8)	4.66
		SET*	3.6	0.36	2.3	17.2 (18.0)	7.65
		HET	0.2	0.13	1.7	21.7 (25.0)	7.36
		64 km/h Cruise	0.05	0.12	1.3	17.8 (22.4)	8.00

---

* Average of 4 tests
** Parenthetical Numbers are % Conversion, Fuel sulfur to sulfate
# Duplicate FTP

Table V-4

Comparison of GM and Perovskite Oxidation Catalysts

Pelletized Catalyst System	Average FTP Gaseous Emission Rates (g/km)		Overall % Conversion	
	CO	HC	CO	HC
GM	3.3	0.25	80	88
Perovskite	7.3	0.41	56	80

The poorer control of the perovskite catalyst is primarily due to a slower rate of catalyst warm-up. Typical conversions are shown in Table V-5 for Bag 1 and Bag 2 of the FTP. On the cold start, the perovskite catalyst converts only 35% CO and 50% HC, compared to 71% CO conversion and 68% HC conversion for the GM catalyst. Although warmed-up conversions are slightly lower for the perovskite catalyst, as evidenced by Bag 2 data, this had little effect on overall vehicle emissions.

Table V-5

Catalyst Conversions

Catalyst	Cold Start Conversion Bag 1 (%)		Warmed-Up Conversion Bag 2 (%)	
	CO	HC	CO	HC
GM	71	68	99	95
Perovskite	35	50	94	91

Sulfate emissions were also higher for the perovskite catalyst. At approximately 6 400 km, the GM catalyst averaged 3.0 mg $SO_4^=$/km for the SET, compared to 17.2 mg $SO_4^=$/km for the perovskite catalyst. Only on the FTP did the perovskite catalyst emit less sulfate than the commercial GM catalyst. During the SET, HET, and cruise, the perovskite catalyst produced 3-5 times as much sulfate as the GM catalyst.

The operating temperatures of both catalyst systems were quite similar. This would be expected, since the vehicle A/F ratio was running lean, approximately 15 to 15.5, so that catalytic conversion of CO would not be a factor influencing operating temperatures. The operating temperatures for both catalyst systems is shown in Table V-6.

Table V-6

Catalyst Temperatures
Standard Vehicle Configuration

Test	Catalyst Temperature, °C Average	 Peak
AMA Durability Cycle	455	550
FTP	425	580
SET	505	540
HET	515	---
64 km/h cruise	480	---

V.5 High Temperature Operation

V.5.1 Vehicle Modifications

Cylinder heads with port liners were installed, and insulation applied to the exhaust manifold and piping to increase the catalyst operating temperatures. A comparison of the catalyst operating temperatures in the standard and high temperature configurations is shown in Table V-7. As seen in this table, operating temperatures were about 200°C higher during the AMA durability cycle, and about 100°C higher during the test sequence.

V.5.2 Comparison of GM and Perovskite Catalyst Gaseous Emissions in the High Temperature Configuration

The gaseous emission data from the higher temperature configuration tests are shown in Table V-8. As in the case of the standard configuration, emissions with the perovskite catalyst were substantially higher than those with the GM catalyst, particularly for the FTP. CO and HC emissions were 17.1 and 0.82 g/km, respectively, for the perovskite catalyst, and 3.7 and 0.36 g/km for the GM catalyst on the FTP. Emissions

TABLE V-7

CATALYST TEMPERATURES
MODIFIED VEHICLE CONFIGURATION

	Catalyst Temperature, °C			
	Average		Peak	
Test	High Temperature System	Standard System	High Temperature System	Standard System
48k Durability Cycle	650	455	740	550
FTP	515	425	550	500
SET	615	505	650	540
HFET	620	515	—	—
64 km/h cruise	600	460	—	—

TABLE [illegible]

COMPARATIVE GASEOUS EMISSIONS UNDER HIGH TEMPERATURE CONFIGURATION CONDITIONS

Vehicle km	Catalyst	Catalyst km	Test	Gaseous Emissions g/km CO	HC	NOx	Fuel Economy km/L
22 408	GM	16 350	FTP	1.7	0.36	1.1	4.69
			SET*	2.9	0.28	1.2	6.57
			HET	0.4	0.21	1.1	7.50
			64 km/hr. cruise	0.03	0.09	0.9	8.45
23 589	[illegible]	7 780	FTP	17.3	0.62	1.5	4.50
			SET*	3.1	0.29	1.5	6.52
			HET	0.5	0.26	1.3	7.28
			64 km/hr. cruise	0.26	0.16	0.9	8.86
21 760	None	- - - -	FTP	20.6	2.67	1.4	4.57

---

* Average of four tests.

on the warmed-up cycles were only slightly higher for the perovskite catalyst, pointing to catalyst warm-up as the major factor in the poorer control for the perovskite catalyst. This is confirmed in Table V-9, which shows the contribution of the cold start, Bag 1, and warmed-up cycles, Bags 2 and 3, to the overall FTP emissions. A comparison between the GM and perovskite catalysts shows the higher cold start emissions with the perovskite catalyst. Since both catalysts see the same nominal exhaust conditions during the cold start, it appears that the lite-off temperature of the perovskite catalyst must be higher than that of the GM catalyst.

V.5.3 Sulfate Emissions from GM Pelletized and Perovskite Oxidation Catalysts in High Temperature Configuration

As expected from thermodynamic considerations, sulfate emissions from both the GM and perovskite catalysts were substantially decreased at the higher catalyst temperatures. Sulfate emissions are shown in Table V-10 for both the test sequences in the high temperature configuration and in the standard configuration that preceded the installation of the port liners and insulation. Sulfate emissions decreased by factors of approximately 2-4 on the GM and perovskite catalysts due to increasing the catalyst temperature 100°C. Significant reductions in sulfate emissions occurred for all test modes. However, the reductions were higher for the warmed-up test modes, i.e., the SET, FET, and 64 km/h cruise. Sulfate emissions from the perovskite catalyst were considerably higher than the GM catalyst. This is consistent with results obtained in the standard configuration.

V.5.4 Comparison of Emissions Between Standard and High Temperature Configurations

It appears that NO_x emissions have decreased due to the addition of port liners. Table V-8 showed the NO_x emissions over the test sequence with port liners and insulation. Compared to the tests without port liners, Tables V-2 and V-3, NO_x emissions have dropped 30-40%. Raw exhaust traces during testing do not indicate any significant changes in carburetion which would account for this NO_x reduction. It is possible that, although the engine is calibrated to run at an A/F of 15-16 during cruise conditions, some cylinders may, at times, receive a rich mixture. This is particularly true during accelerations where power enrichment can occur. Under rich conditions, the port liners may act as a reduction catalyst. NO_x reduction with stainless steel reactors has been reported in the literature. This may account for the reduced NO_x emissions with port liners.

TABLE V-9

AVERAGE FTP GASEOUS EMISSIONS

Configuration	Catalyst	Overall		Gaseous Emissions, g/km			
				Bag 1		Bag 2 & 3	
		CO	HC	CO	HC	CO	HC
Standard	None	16.6	2.07	7.2	0.44	9.4	1.63
	GM	3.3	0.25	2.3	0.15	1.0	0.10
	Perovskite	7.3	0.41	4.9	0.23	2.4	0.18
High	None	20.6	2.67	13.6	0.71	7.0	1.95
Temperature	GM	3.7	0.36	2.8	0.21	0.9	0.15
	Perovskite	17.3	0.62	15.9	0.43	1.4	0.19

TABLE V-10

COMPARATIVE SULFATE EMISSION RATES OF THE GM AND PEROVSKITE CATALYSTS IN STANDARD AND HIGH TEMPERATURE CONFIGURATIONS

GM Catalyst

Test	Standard Configuration		High Temperature Configuration	
	$SO_4^=$ (mg/km)	Conversion (%)	$SO_4^=$ (mg/km)	Conversion (%)
FTP	6.7	4.9	4.6	3.4
SET*	5.6	5.8	1.8	1.9
HET	6.0	8.0	1.6	1.9
64 km/h Cruise	8.4	10.6	1.9	2.5

Perovskite Catalyst

Test	Standard Configuration		High Temperature Configuration	
	$SO_4^=$ (mg/km)	Conversion (%)	$SO_4^=$ (mg/km)	Conversion (%)
FTP	6.6	4.8	3.1	2.2
SET*	17.2	18.0	7.4	7.6
HET	21.7	25.0	8.5	9.7
64 km/h Cruise	17.8	22.4	8.8	12.2

---

*Average 5 tests

A comparison of the vehicle FTP emissions, both with and without catalysts, in the standard and high temperature configurations is shown in Table V-9. HC emissions have been increased significantly by the addition of port liners and insulation. This applies both with and without catalysts. The increase in HC emissions is probably too great to be attributed to test variability. CO emissions increased significantly only for the perovskite catalyst. Although the CO emissions are higher with no catalyst and the GM catalyst in the high temperature configuration, these differences are within test variability. This may indicate that the perovskite catalyst lost activity during kilometer accumulation in the high temperature configuration. This loss in activity appears to be only during the cold start, since Table V-9 indicates that warmed-up CO emissions did not increase for the perovskite catalyst.

The increase in HC emissions in the high temperature configuration appears to be due to a slower rate of engine warm-up. Table V-9 shows that HC emissions are considerably higher only during the cold start. A slower rate of engine warm-up would increase HC emissions and is consistent with the addition of port liners. The port liners reduce the heat transfer from the exhaust to the engine coolant in the area of the exhaust port. This reduction in heat transfer results in the engine requiring more time to reach normal operating temperatures. HC emissions are known to be increased at operating temperatures significantly below normal. Even though catalyst warm-up should be increased by the addition of the port liners, the increased warm-up rate did not compensate for the increased HC emissions in the high temperature configuration. An alternative explanation for the increased HC in the high temperature configuration could be a longer choke action. However, raw exhaust traces indicate that the choke action was not appreciably affected by the addition of the port liners and insulation.

It should be pointed out that the increased HC found with port liners in this case does not appear to be universal. Other workers have reported reductions in HC emissions with port liners in thermal reactor systems. Possibly the lack of a thermal reactor in our vehicle accounts for the difference in results.

V.6 Comparison of Perovskite Monolithic Catalysts with Engelhard PTX-IIB

V.6.1 Test Procedure

The test vehicle used for the pelletized catalysts was also used for the test sequence with the monolithic catalysts. All tests with the monolithic catalysts were with the vehicle in its high temperature configuration. To establish a basis for comparison, a fresh

Engelhard monolithic catalyst was tested, along with the perovskite monolith. In both cases, the catalysts were not conditioned, but were tested at zero kilometers.

V.6.3 Emission Results with Monolith Catalysts

The DuPont monolith provided poorer control of CO and HC than the Engelhard catalyst. CO and HC FTP emissions for the DuPont catalyst were 6.83 and 0.61 g/km, as opposed to 1.08 and 0.15 g/km, respectively, for the Engelhard monolith. On the SET's, the DuPont catalyst averaged 4.15 g/km CO and 0.5 g/km HC, the Engelhard catalyst 0.7 g/km CO and 0.16 g/km HC. The emissions data for these two catalyst systems are given in Tables V-11 and V-12.

Table V-11

Emission Characteristics, Vehicle Equipped with Monolithic Perovskite Catalyst in High Temperature Configuration

Test	Emission Rate, g/km			
	CO	HC	NO_x	H_2SO_4*
FTP	6.83	0.61	3.31	0.034 (22)
SET	4.94	0.55	3.05	0.024 (22)
SET	4.27	0.44	3.02	0.003 (3)
FET	1.61	0.43	2.63	0.003 (4)
SET	4.11	0.48	3.03	0.003 (3)
SET	3.14	0.36	3.15	0.002 (2)
64 kph, 1 hr	0.09	0.22	1.73	0.003 (4)

* Bracketed numbers are % conversion of fuel sulfur to sulfate, based on emitted sulfate.

Initial sulfate emissions were higher with the DuPont monolith; but SO_2 conversions averaged about 3% on the last five runs of the test sequence. Conversions with the Engelhard system averaged (first six runs) about 7.3%. The Engelhard system exhibited considerably higher sulfate emissions on the 64 km/h cruise, 0.026 g/km of H_2SO_4, corresponding to 30% conversion. The sulfate emission results are shown in Tables V-11 and V-12.

Table V-12

Emission Characteristics, Vehicle Equipped with Engelhard Monolithic Oxidation Catalyst in High Temperature Configuration

Test	Emission Rate, g/km			
	CO	HC	NO_x	H_2SO_4*
FTP	1.08	0.15	3.03	0.009 (6)
SET	1.63	0.09	1.00	0.009 (8)
SET	0.63	0.22	2.99	0.004 (4)
FET	0.60	0.24	2.66	0.009 (9)
SET	0.46	0.08	2.82	0.010 (11)
SET	0.89	0.25	2.68	0.008 (7)
64 kph, 1 hr	0.08	0.04	1.60	0.026 (30)

* Bracketed numbers are % conversion of fuel sulfur to sulfate, based on emitted sulfate.

These results indicate that the monolithic DuPont catalysts are a lower emitter of sulfate than their pelletized counterpart. However, due to its poorer control of CO and HC compared to commercial catalysts, no further work is planned with the DuPont monolith.

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APPENDIX A

Selection of Calcium, Silica, and Alumina Components for Physical Combinations

1. Calcium Hydroxide

Calcium hydroxide (technical grade) is agglomerated by slowly adding water to powdered calcium hydroxide while stirring slowly in a mixing apparatus. A quantity of 400 g of calcium hydroxide is mixed with approximately 200 g of distilled water for the agglomeration. The product is dried in an oven at 65°C to a moisture content of approximately 10 wt % and passed through a 14 mesh screen. Final moisture content is determined by drying a sample for four hours at 110°C and calculating the percent of weight loss.

2. Calcium Oxide

Source: Pfizer Incorporated
Mineral, Pigments, and Metals Division

Description: "High Calcium Granular Quicklime"
10-100 mesh
94.0-96.0% CaO, balance inert

Before use this material is screened to remove particles larger than 14 mesh (0.0469 in., 1.19 mm).

3. Calcium Carbonate

Source: Pfizer Incorporated
Mineral, Pigments, and Metals Division

Description: "Neico High Calcium Limestone, ATF-20"
20+ mesh
94.0-96.0% $CaCO_3$, balance inert

4. Silica

Source: PPG Industries, Incorporated

Description: "Hi-Sil 210 Hydrated Amorphous Silica"
94 wt % SiO_2, balance inert

5. Alumina

Source: Aluminum Company of America

Description: Alcoa Hydrated Alumina C-31 (coarse)
64.9 wt % Al_2O_3 equivalent
(calculated for $Al_2O_3 \cdot 3H_2O$ or $Al(OH)_3$,
Al_2O_3 = 65.4 wt. %)

APPENDIX B
TABLE B-1

PHYSICAL COMBINATIONS - DRY MIXTURES;

PELLETING TRIALS

Composition, Wt %	1	2	3	4	5	6	7	8	9
Calcium Hydroxide (1)	85	85	85	-	-	-	-	-	-
Calcium Oxide (2)	-	-	-	85	85	85	-	-	-
Calcium Carbonate (3)	-	-	-	-	-	-	85	85	85
Silica (4)	15	-	7.5	15	-	7.5	15	-	7.5
Alumina (5)	-	15	7.5	-	15	7.5	-	15	7.5
Sterotex (6)	-	-	-	+2%	+2%	+2%	+2%	+2%	+2%
Operation During Pelleting									
Flow into dies:	fair	fair	fair	good	good	good	good	good	good
Ease of compaction/ ejection:	fair	fair	fair	poor	difficult	poor	poor	poor	poor
Crush Strength of 3.2 cm Pellets									
Initial Crush Strength (kg)	2.7	3.5	2.9	too soft	2.6	0.6	0.2	0.6	0.1
Crush Strength after 16 hrs @ 315°C (kg) (7)	4.1	4.5	4.4	powdered	powdered	powdered	0.2	0.2	0.1
Notebook Reference 4349 -	33-1	33-2	33-1	32-1	32-2	32-3	34-1	34-2	34-3

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(1) Calcium hydroxide is wet granulated, dried at 65°C, and passed through a 14 mesh screen. Final moisture content = 15 wt %. In formulating, the weight of granular calcium hydroxide is adjusted to allow for the moisture content.

(2) Pfizer High Calcium Granular Quicklime, 14-100 mesh. After mixing with binder these formulations were reground and screened to 20+ mesh.

(3) Pfizer Belco High Calcium Limestone, ATF-20, 20+ mesh. After mixing with binder these formulations were reground and screened to 20+ mesh.

(4) Hi-Sil 210 Hydrated Amorphous Silica, 94 wt % SiO_2.

(5) Alcoa Hydrated Alumina C-31 (coarse), 64.9 wt % Al_2O_3 equivalent. In formulating,weight of Alcoa C-31 is adjusted to give the required concentration of Al_2O_3.

(6) Sterotex, lubricant for tablet making, Capital City Products Company, Columbus, Ohio.

(7) The pellets are heated in an oven 46 h at 95°C, then 6 h at 150°C, followed by 16 h at 315°C.

APPENDIX B
TABLE B-2

Preparation of Chemical Combinations By Coprecipitation

1. "Tricalcium Silicate," $(CaO)_3\ SiO_2$

Calculated for $(CaO)_3\ SiO_2$:

CaO = 73.68 wt %

SiO_2 = 26.32 wt %

Materials: $Ca(NO_3)_2 \cdot 4H_2O$, reagent grade, 1018 g = 4.31 moles

$Na_2SiO_3 \cdot 9H_2O$, reagent grade, 400 g = 1.44 moles

$NaOH$, 50 wt % solution, 460 g = 5.75 moles

Procedure:

The calcium nitrate is dissolved in 3 litres of distilled water in a 10 litre jar. A solution is made of the sodium metasilicate in 700 ml of distilled water to which is added the sodium hydroxide solution. The combined solution is added to the calcium nitrate solution via an addition funnel over one hour. The resultant mixture is stirred for an additional 30 minutes and filtered by vacuum using a large Büchner funnel. The filter cake is washed four times with 1000 ml of distilled water, dried in an oven at 65°C for 20 hours, and screened to 14-35 mesh.

NBR-4349-28

2. "Tricalcium Aluminate," $(CaO)_3\ Al_2O_3$

Calculated for $(CaO)_3\ Al_2O_3$:

CaO = 62.25 wt %

Al_2O_3 = 37.75 wt %

Materials: $Ca(NO_3)_2 \cdot 4H_2O$, reagent grade, 859 g = 3.64 moles

Nalco No. 5, solution of sodium aluminate, $Na_2Al_2O_4$; (equivalent wt % Al_2O_3 = 26.4, wt % $NaOH$ = 24.4) use 468 g (= 1.21 moles Al_2O_3 + 2.85 moles $NaOH$)

$NaOH$, 50 wt % solution, 353 g = 4.41 moles

Procedure:

The calcium nitrate is dissolved in 4 litres of distilled water in a 10 litre jar. The Nalco No. 5 and sodium hydroxide solutions are mixed in an addition funnel and added to the calcium nitrate solution with rapid stirring over 30 minutes. The mixture is stirred for an additional 30 minutes, filtered by vacuum through a large Buchner funnel. The filter cake is washed four times with 1000 ml of distilled water, dried in an oven at 65°C for 20 hours, and screened to 14-35 mesh.

HBR-4349-30

3. "Tricalcium Aluminosilicate," $(CaO)_3\,(Al_2O_3 \cdot SiO_2)_{1/2}$

Calculated for $(CaO)_3\,(Al_2O_3 \cdot SiO_2)_{1/2}$

CaO = 67.48 wt %

SiO_2 = 12.05 wt %

Al_2O_3 = 20.47 wt %

Materials: $Ca(NO_3)_2 \cdot 4H_2O$, reagent grade, 1423 g = 6.03 mole

$Na_2SiO_3 \cdot 9H_2O$, reagent grade, 285 g = 1.00 mole

Nalco No. 5, solution of sodium aluminate, 388 g = 1.00 mole Al_2O_3 + 2.37 mole NaOH

NaOH, 50% solution, 614 g = 7.68 mole

Procedure:

The calcium nitrate is dissolved in 4 litres of distilled water in a 10 litre jar. The sodium metasilicate is dissolved in 800 ml of distilled water and mixed with 307 g of 50% sodium hydroxide solution in an addition funnel. In a second addition funnel the Nalco No. 5 is mixed with the remaining 307 g of 50% sodium hydroxide, plus 250 ml of distilled water to make the liquid volumes equal in the two addition funnels. The contents of the two addition funnels are simultaneously added to the calcium nitrate solution over a period of 30 minutes with rapid stirring. Stirring is continued for 30 minutes. The mixture is filtered by vacuum using a large Buchner funnel. The filter cake is washed four times with 1 litre of distilled water, dried in an oven at 65°C for 20 hours, and screened to 14-35 mesh.

HBR-4349-41

APPENDIX B

TABLE B-3

PRESSURE DROP ACROSS $SO_4^=$ TRAP

Benchmark Rings (12.7 mm OD)

Kilometre	ΔP, kPa Idle	ΔP, kPa 64 km/h
0	0	0,5
6 400	0,5	0,9
16 000	0,5	1,0

Benchmark Pellets (4.76 mm OD)

Kilometre	ΔP, kPa Idle	ΔP, kPa 64 km/h
0	0	1,0
5 000	0,5	1,2
15 000	0,7	1,0

Ca(OH)2/Dicalite Pellets (4.76 mm OD)

Kilometre	ΔP, kPa Idle	ΔP, kPa 64 km/h
0	0,2	0,75
5 000	0,2	0,5
15 000	0	0,75

APPENDIX C

MEASUREMENT TECHNIQUES

C.1 Gaseous Emissions

Gaseous emissions were measured using standard instrumentation for Federal Emission Test Procedures. CO and CO_2 were analysed by NDIR, hydrocarbons by FID, and NO_x by chemiluminescence.

C.2 Measurement of Sulfate Emissions

Sulfate emission samples were collected using Exxon Research's exhaust particulate sampling system. The sulfate content of samples collected was determined by titration of sulfate to the thorin end point using an automatic recording titrator and a probe colorimeter.

C.2.1 Exhaust Particulate Sampling System

The exhaust particulate sampling system has been designed to collect particulate matter at constant temperature during the 1972 and 1975 Federal Test Procedure, and 64 km/h (40 mph) cruise conditions. This system is capable of frequent and convenient operation, and is compatible with constant volume sampling (CVS) of auto exhaust. Compatibility is obtained because the particulate sampler requires only a small portion of the diluted exhaust, the major portion of the sample is available to the CVS system for the measurement of gaseous emissions. Conditions used in the measurement of exhaust particulate conform to those mandated by the Federal Test Procedures for gaseous emissions.

This sampling system uses a small tunnel which means that low dilution ratios are used, allowing gaseous emissions such as CO, hydrocarbons, NO_x and SO_2 to be measured accurately. While low dilution ratios are desirable from the standpoint of CVS gaseous emission measurements, the collection of a proportional sample of particulate matter at constant temperature 32°C (90°F) from a sample stream having a high dew point without causing condensation of water requires an advanced temperature control system.

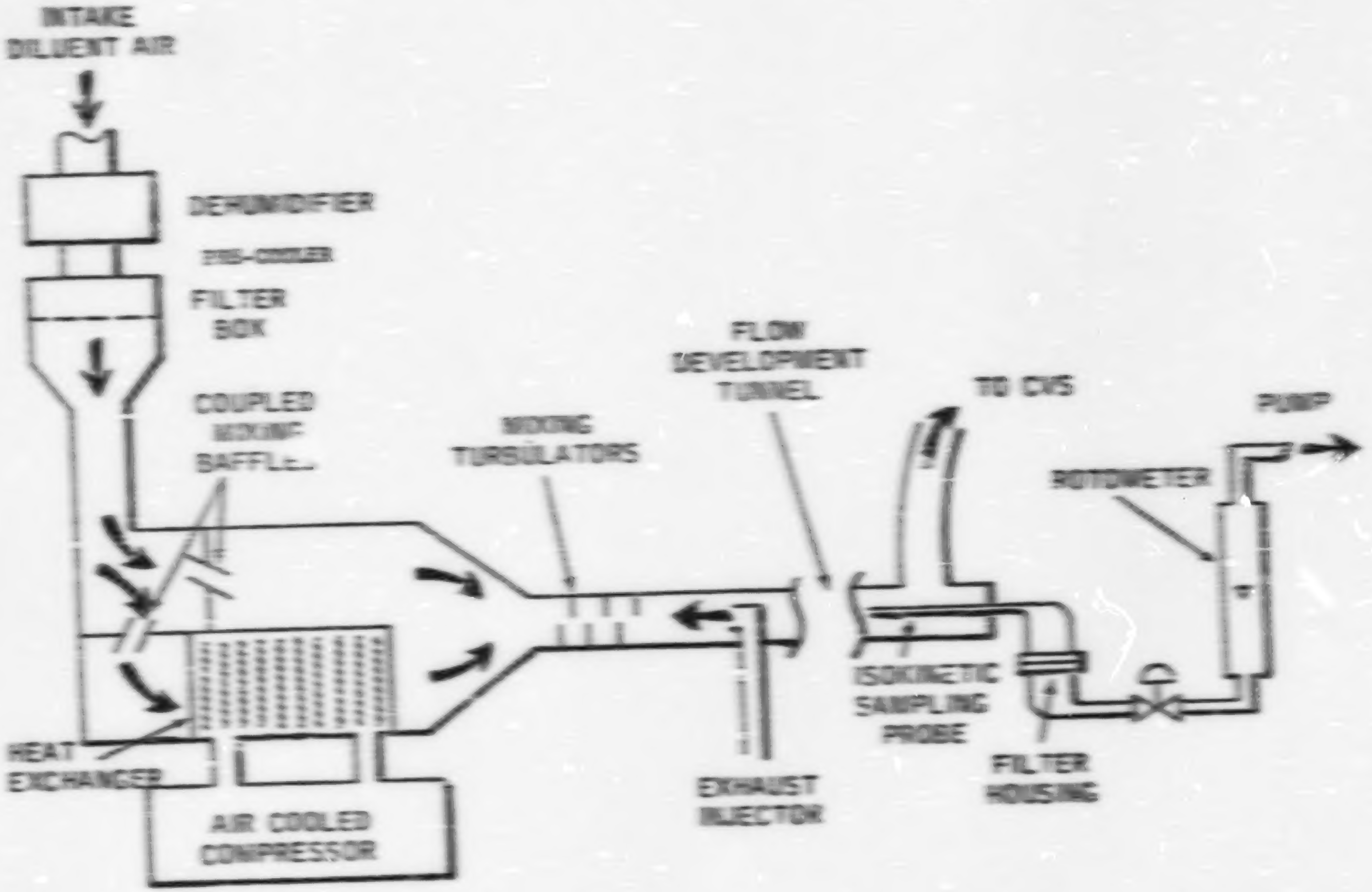
C.2.1.1 Sampling System Components

The particulate sampler which has been discussed previously (8) is shown schematically in Figure C-1. This system has five major components:

1. A diluent air preparation system
2. A flow development tunnel
3. An exhaust injector system
4. An isokinetic sampling probe
5. A particulate measuring device, which in the case shown is a 0.2 micron glass fiber filter

FIGURE C-1

EXHAUST PARTICULATE SAMPLER



The overall function of this system is to allow the collection of particulate matter from an isokinetically sampled portion of diluted exhaust which has been cooled to 32°C by dilution with chilled, dehumidified, filtered air. The function of each of the components in accomplishing this objective is described below.

C.2.1.2 Diluent Air Preparation System

This system consists of a dehumidifier, filter, coupled mixing baffles, a cooling system, and mixing turbulators.

The dehumidifier shown schematically in Figure B.2 minimizes the possibility of condensation occurring in the sampling system during a run, and is an integral part of the temperature control system. Diluent air is dried by passage through a filter and a slowly rotating desiccant wheel containing laminated flat and corrugated asbestos, impregnated with a regenerable desiccant, LiCl. Dehumidification of diluent air and desiccant reactivation are concurrent processes, so that dehumidification can be carried out on a continuous basis. The dehumidifier, a Honeycombe Model HC 750-EA is manufactured by Cargocaire Engineering Corporation and described in their Bulletin No. 07169(9).

Dehumidified inlet air passes from the dehumidifier to a filter box containing a paper filter, a bed of activated charcoal, and a second paper filter. This assembly is the standard filter box assembly for the Scott Research Constant Volume Sampler (CVS) unit. The filter assembly removes the particulate matter present in the diluent air and reduces and stabilizes the background hydrocarbon content of the diluent air.

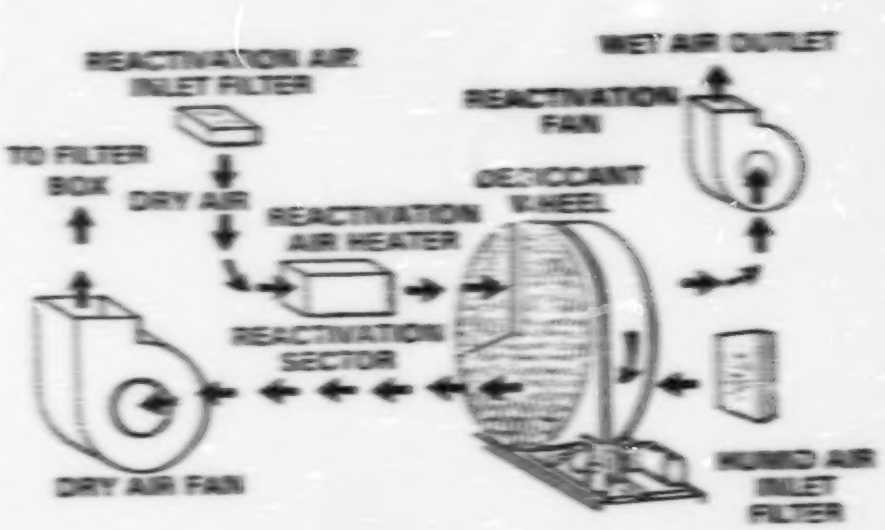
Because regeneration of the desiccant is accomplished by heating, the dehumidified air emerging from the drum is above ambient temperature. A pre-cooler situated between the dehumidifier and the CVS filter cools the dehumidified air stream down to ambient temperature to take the additional cooling load imposed by the dehumidification step away from the final cooling system. The pre-cooler consists of several rows of coils through which chilled city water is passed.

The coupled mixing baffles continuously divide the dehumidified, filtered air into two portions, one which passes through the cooling system, and a second portion which bypasses the cooling system. The position of the mixing baffles is controlled by a rapid response, deviation-type controller operating on an input signal from a thermocouple in the filter housing. The system is designed to maintain 32°C at the filter housing, during the 1972 or 1975 Federal Test Procedures, and 64 km/h cruise.

The controller operates by comparing an input signal from a thermocouple in the filter housing with a set point signal, and takes corrective action to either raise or lower the output signal until the set point and thermocouple input are equal. The controller used was an Electronic Control System Model 6700 Controller(10). The output signal

FIGURE C-2

SCHEMATIC OF DEHUMIDIFICATION SECTION



from the controller is fed to an electric to pneumatic transducer (11) which in turn activates a pneumatic controller(12) which operates the coupled baffles.

The cooling system is an air cooled condensing evaporator which has a cooling capacity of 8,330 kcal/hr. The evaporator is a Dunham-Bush, Model PCO-500 unit(13) containing ten rows of custom-made cooling coils (14).

The mixing turbulators insure that chilled air is thoroughly mixed with the portion of air bypassing the cooling system before the stream is used to dilute the vehicle exhaust. The turbulators consist of six semi-circular perforated plates attached to a 1/2" diameter wall tube at their centers, arranged in a helical series sequence along the tunnel axis. This arrangement allows both longitudinal and latitudinal mixing.

Maximum flow through the diluent air preparation system is determined by the cooling capacity of the chiller. Presently, this limitation is about 13 m^3/min.

C.2.1.3 Flow Development Tunnel

The exhaust and diluent air are mixed and a uniform velocity profile is developed in the flow development tunnel. The flow development tunnel is a 2.23 m long section of a 4-inch diameter Schedule 5 (actual I.D. = 11.0 cm) stainless steel pipe. Neither the length nor the diameter of the flow development tunnel have been optimized, but as will be shown in another section, a dilution tunnel of these dimensions is satisfactory for this purpose.

C.2.1.4 The Exhaust Injection System

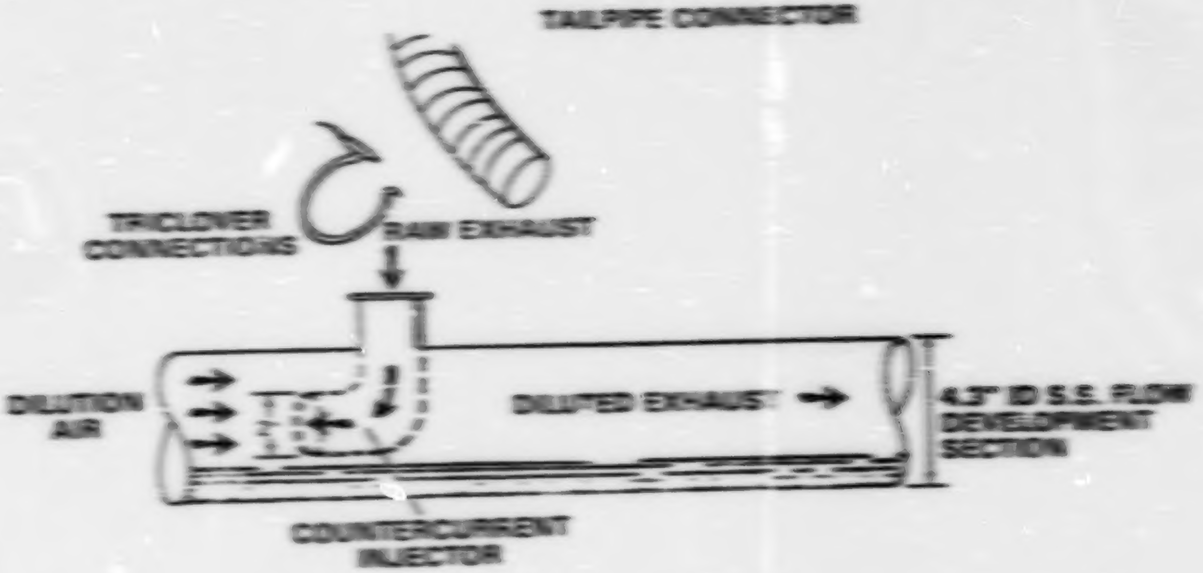
The raw exhaust is mixed with the diluent air normally used in the CVS in such a way as to completely mix the two in as short a time interval as possible. This is accomplished by injecting the exhaust in a countercurrent direction to the diluent air stream. Previous experiments (8) have shown this to be the most efficient way of obtaining a rapidly mixed, uniformly distributed diluted exhaust sample stream. Figure B-3 shows a schematic of the exhaust injector in the countercurrent position.

C.2.1.5 Isokinetic Probe

Isokinetic sampling is required to insure that the particulate sampled is representative of the particulate in the main stream; that is, the particulate concentration and size distribution in the probe sample should correspond to that of the main stream. The probes are designed so that the sample stream is divided into two parts with a volume ratio equal to the ratio of the cross-sectional areas of the openings of the sample probes and the tunnel cross-sectional area, that is

FIGURE 6-3

COUNTER CURRENT EXHAUST INJECTION SYSTEM



$$\frac{\text{Area (probe)}}{\text{Area (tunnel)}} = \frac{\text{Flow Rate in SCFM (probe)}}{\text{Flow Rate in SCFM (tunnel)}}$$

Another problem to be considered in probe designs is minimizing sample deposition in the probes. When suspended particulate matter leaves the tunnel and enters the sampling probe, it is leaving a low surface to volume region and entering a high surface to volume region. Relative sample losses by impaction should be greater in the probe than in the tunnel. Therefore, the probe should be as short and direct as possible to minimize the residence time of the particulate matter in the probe. The filter housing connected to the probe is flared out as soon as physically possible to minimize the surface to volume ratio of the housing and thereby reduce sampling losses by impaction in this portion of the sampling system.

C.2.1.6 Particulate Collecting Stage

At present, particulates are collected by filtering the sample through pre-weighed filters. In principle, other particulate collectors such as impactors and other devices, could be utilized with the particulate sampling system. In this paper, total particulates are determined gravimetrically using Gelman Type E glass fiber filters which have an effective porosity of 0.2 microns.

C.2.2 Exhaust Particulate Sampling System Performance

In order to function properly for sulfate emissions, the exhaust particulate sampling system should have the following capabilities:

(1) mix exhaust and diluent air rapidly,
(2) allow development of a uniform velocity profile in the flow development tunnel,
(3) minimize sampling losses in the tunnel,
(4) give equivalent emission rates with parallel filters, and
(5) maintain constant temperature at the particulate collecting stage.

All of the above have been adequately documented (8) and will be reviewed in this section.

C.2.2.1 Rapid Mixing of Exhaust and Diluent Air

Three methods of injecting exhaust into diluent air were tested: co-current flow, perpendicular flow, and countercurrent flow. In each case, the exhaust was injected through a 5.1 cm O.D. x 0.089 cm wall stainless steel tube into the flow development tunnel. The efficiency of the three injection methods was tested by measuring hydrocarbon concentrations in the diluted exhaust at a point approximately 2.23 m downstream of the injection point. Hydrocarbons were chosen as the tracer because they are easier to measure than particulates. If the gaseous components of the exhaust are not evenly distributed over the flow cross-section, there is no reason to believe that the particulates will be well distributed. The ultimate test of uniformity of particulate distribution in the tunnel is the consistent attainment of equivalent particulate emission rates with parallel filters. The results showed that uniform distribution was obtained only by countercurrent injection.

C.2.2.2 Development of Uniform Flow in Flow Development Tunnel

To insure that samples taken at any point in the tunnel cross-section will contain the same amount of particulate material, a uniform radial distribution of particulate material in the tunnel must be obtained. The small size of the tunnel would make it difficult to obtain reliable measurements of velocity profiles. However, it is well known that the higher the Reynolds Number of turbulent flow, the flatter the velocity profile (15). However, over the range of interest for this system, the effect of this flattening of the velocity profile is negligible. Consider the system as having a flow of air at 32°C through a 11 cm diameter pipe.

$$N_{Re} = \frac{D\overline{U}\rho}{\mu} \qquad (1)$$

where N_{Re} = Reynolds Number

D = pipe diameter = 11.0 cm = 0.110 m

$\overline{U}$ = average fluid velocity = $\frac{4\,(13)}{\pi\, D^2}$ = 1370 m/min

8.21 x 10^4 m/hr.

ρ = density = 11.14 kg/m^3

μ = fluid viscosity = 0.186 cp = 0.670 kg/m-hr.

$$N_{Re} = \frac{(0.110\ \text{m})\ (8.2 \times 10^4\ \text{m/hr})\ (1.14\ \text{kg/m}^3)}{0.670\ \text{kg/m-hr}} = 154{,}000$$

Equation (1) shows that the Reynolds Number varies inversely with diameter for constant volumetric flow. Therefore, decreasing pipe diameter to 2.5 cm would increase N_{Re} to 615,000 while increasing pipe diameter to 40 cm would decrease N_{Re} to 40,000.

One measure of the flatness of the velocity profile is the ratio of the mean gas velocity to the maximum gas velocity. It has been shown experimentally that for turbulent flow in smooth pipes (15)

$$\frac{u}{U} = \left(\frac{Y}{R}\right)^{1/N} \qquad (10)$$

where u = point velocity
U = maximum velocity at center
Y = distance from the wall
R = pipe radius, and
N = a constant depending on Reynolds Number

Schlicting (9) shows that average velocity $\bar{u}$ is,

$$\bar{u} = \frac{2N^2}{(N+1)(2N+1)} \qquad (3)$$

The following table shows that the effect of changing pipe diameter over a large range would be negligible.

Effect of Reynolds Number
on Velocity Profile

N_{Re}	N	$\bar{u}/U$
23,000	6.6	.807
110,000	7.0	.816
500,000	8.0	.837

Another important factor in choosing the diameter of the flow development tunnel is its effect on the length of the tunnel and the diameter of the probes. As a general rule, ten pipe diameters are usually sufficient to develop a fully turbulent velocity profile. The larger the diameter, the longer the tunnel required and the longer the residence time in the flow development section. Longer residence time leads to higher particulate settling and greater inaccuracy in the measurement. Therefore, the tunnel diameter should be minimized. However, as tunnel diameter decreases, the pressure drop through the tunnel increases and the size of the probes needed for isokinetic sampling decreases. The problems caused by high pressure drop are obvious. Smaller diameter probes should be avoided since they provide higher surface to volume ratios and result in more loss of particulate by impaction. The 11 cm diameter pipe in use offers a reasonable compromise between these various factors.

C.2.2.3 Tunnel Sampling Losses

Particulate deposition in the flow development section was measured by introducing an artifically produced mono-disperse (3.5 micron diameter) methylene blue aerosol into the exhaust injector in the same manner as for auto exhaust. The system was disassembled after the run, the tunnel surface washed with methanol and the washings analyzed spectrophotometrically. The sensitivity of the method for methylene blue is in ppb range. Analysis showed that tunnel losses are small, amounting to less than 1% of the total aerosol introduced. No dye was detected in the tunnel section housing the exhaust injector. About 0.1% of the aerosol was deposited in the tunnel mid-section, and about 0.3% was deposited in the tunnel section housing the probes. Independent tests by U. S. Environmental Protection Agency workers with a tunnel of similar dimensions have confirmed our results regarding tunnel sampling losses (3).

C.2.2.4 Equivalent Emission Rates with Parallel Filters

Since only a small fraction of the diluted exhaust is sampled for the particulate analysis, at least two parallel probes coupled to the appropriate filters are needed to serve as internal checks on the sampling system. One method of determining whether proper sampling is achieved relies on the ratio of the weight of particulate collected (W_A) by filter A, and the volume flow rate (F_A) through probe A. This ratio should equal the corresponding ratio of these parameters for filter B and probe B, that is:

$$\frac{W_A}{F_A} = \frac{W_B}{F_B} = \frac{W_C}{F_C} = \text{etc.}$$

The particulate emission rates in grams/kilometer (g/km) should be the same for all filters in a given run since

$$\frac{g}{km} = \frac{W_A}{F_A}\;\frac{F_P}{\Delta km} = \frac{W_B}{F_B}\;\frac{F_P}{\Delta km} = \text{etc.}$$

where F_P is the volume flow rate through the tunnel and Δkm the distance in kilometers accumulated on the particular test procedure.

Excellent agreement between parallel filters has been obtained using this sampling system with conventional and catalyst-equipped vehicles operating on a variety of unleaded fuels under cyclic and state test conditions. Partial documentation of this agreement has been previously described (8).

C.2.2.5 Temperature Maintenance of the Particulate Collection Stage

The dehumidifier is a key component of the temperature control system, particularly since the sampling system is one in which the air/exhaust dilution ratios are low, unlike other particulate sampling systems (16,17). This means that the relative humidity of the diluent air is a key parameter. For example, during the steep acceleration portion of the Federal Test Procedure, the exhaust volume flow rate from a vehicle equipped with a 350 CID V-8 engine may be as high as 3.4 m^3/min. This means that dilution ratio would drop below 4 in the sampling tunnel. If the relative humidity of the diluent air was high, attempts to control the filter temperature at 32°C would result in condensation of water vapor, with the associated loss of particulate matter. This is shown in Figure C-4 which depicts mixture dew point-dilution ratio dependence as a function of the relative humidity of the diluent (24°C) air.

The key role of the dehumidifier can readily be seen. If the relative humidity of the diluent air is low, e.g., below 50%, it should be possible to maintain a 32°C filter temperature without condensation occurring. It can also be readily seen that in the absence of the dehumidifier, on humid days, the dew point of the mixture would exceed 32°C at dilution ratios as high as four, so that condensation would invariably occur during the acceleration portions of the driving cycle.

Attempts to control filter temperatures by omitting the dehumidification step and chilling the diluent air would be difficult to accomplish since water condensing on the coils would feed back latent heat, decreasing the efficiency of the cooler. Continued running would probably result in the condensed water freezing on the heat exchangers, rendering them inoperative.

Figure C-5 shows a typical trace of the relative humidity of the diluted exhaust in the vicinity of the sampling probes during FTP operation with a catalyst-equipped vehicle. This trace is obtained by withdrawing a sample just above the sampling probes and filtering it prior to monitoring the humidity. Filtration is necessary in order to protect the rapidly responding humidity sensor (18).

It is evident that the relative humidity in the region of the probe closely parallels the changes in the cycle driving patterns. At no point in the driving cycle does the relative humidity at the probes reach the saturation level at 32°C. As the relative humidity is lower upstream, condensation in the tunnel upstream of the probe does not occur.

Figure C-6 shows the temperature-time trace at the filter during the above run which is a typical case. A total flow rate of about 13 m^3/min. was used. A 1.2 m long x 5 cm I.D. finned tube between the tailpipe and the exhaust injector was needed to suppress temperature spikes

FIGURE C-4

DEW POINT OF DILUTED EXHAUST VS. AIR/EXHAUST DILUTION RATIO

At Indicated Relative Humidities of 24°C Dilution Air

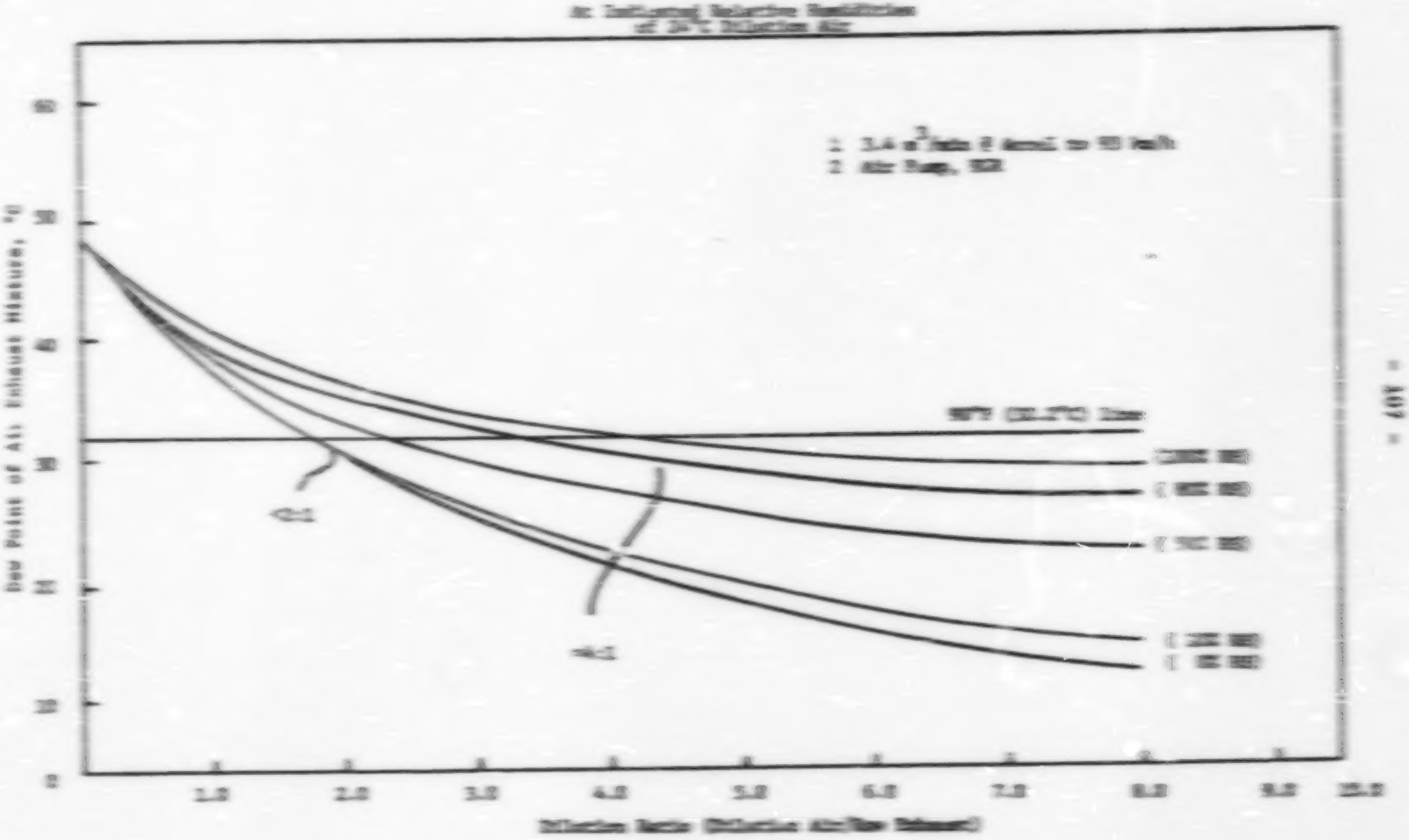


FIGURE C-5

RELATIVE HUMIDITY OF EXHAUST DILUTION AIR
MIXTURE AT VICINITY OF SAMPLING PROBES DURING
THE 1972 FEDERAL TEST—DRIVING CYCLE

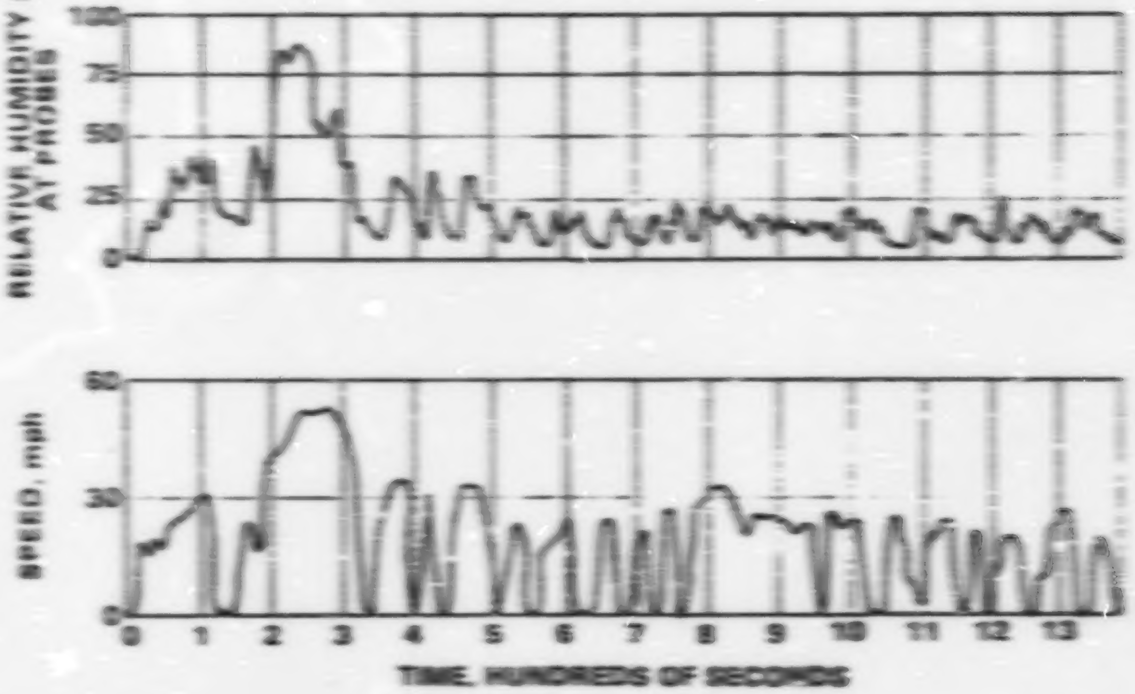
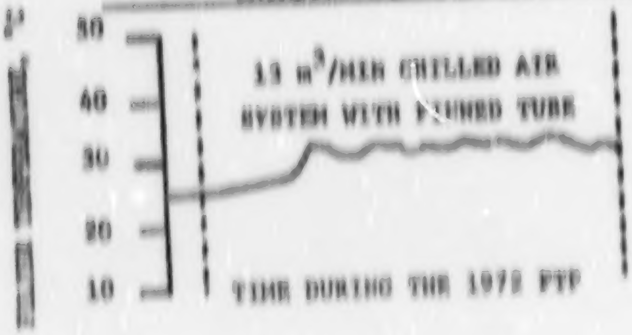


FIGURE C-6

TEMPERATURE CONTROL SYSTEM PERFORMANCE - CATALYST-EQUIPPED CAR



above 32°C during the steep acceleration portion of the driving cycle. It should be noted that the system is designed to prevent temperature excursions above 32°C, not to maintain that temperature during the course of the entire run.

Figure C-7 is a typical relative humidity-time trace for a 64 km/h steady state cruise experiment. The relative humidity surges to about 25% on start up and slowly decreases with running time.

Complete temperature control can be obtained at 64 km/h encapsulating the finned tube in a 10 cm diameter metal cylinder through which ambient air is pumped in a countercurrent direction to the flow of raw exhaust. Figure C-8 shows a schematic of this additional temperature control feature. Encapsulating the finned tube is not necessary for the driving cycle. At the 64 km/h cruise, however, the temperature would slowly rise above 32°C after about 20 minutes if the finned tube was not encapsulated.

C.3 The Goksøyr-Ross Technique

This technique (21) involves passing a sample of exhaust through a condenser maintained between 60 and 90°C. This is above the dew point of the H_2O in the exhaust, but below the dew point of the H_2SO_4 in the exhaust. As a result, H_2SO_4 is condensed in the coil, but H_2O which might catch SO_2, is not condensed.

In our configuration, a modified 300 mm Graham Condenser, equipped with a 60 mm diameter medium porosity fritted glass filter, is used. This unit has been found to give better than 95% collection efficiency at flow rates up to 4 litres/min. Precautions must be taken, however, with regard to the temperature of the incoming gas. If it is too hot, the coil will not provide sufficient cooling to condense all the acid. If the gas is too cool, some may condense out upstream of the coil. The sample lines leading to the condenser must also be chosen with care, to avoid possible reaction with sulfate. Glass or quartz lines are best, but if this is impossible, and mechanical considerations demand the use of metal lines, only tubing which has been passivated by prior exposure to H_2SO_4 containing gases should be used.

After sampling, the condenser coil and glass frit are emptied and rinsed thoroughly. The total liquid is diluted to a standard volume and analysed for sulfate by the Thorin method described in Section C.5.

C.4 The TECO Sulfur Dioxide Analyser

This device (19) operates on a pulsed-fluorescence UV absorption principle as follows. A gas sample is submitted to a source of pulsed ultraviolet light through a monochromatic filter. Sulfur dioxide

FIGURE C-7

RELATIVE HUMIDITY OF EXHAUST DILUTION
AIR MIXTURE AT VICINITY OF SAMPLING
PROBES DURING 64 km/h CRUISE CONDITIONS
at 32°C

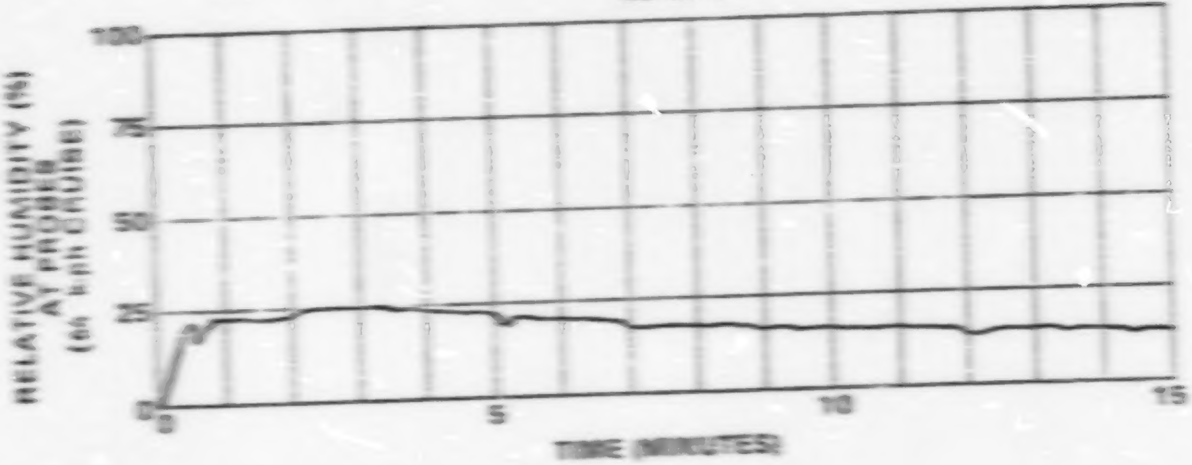
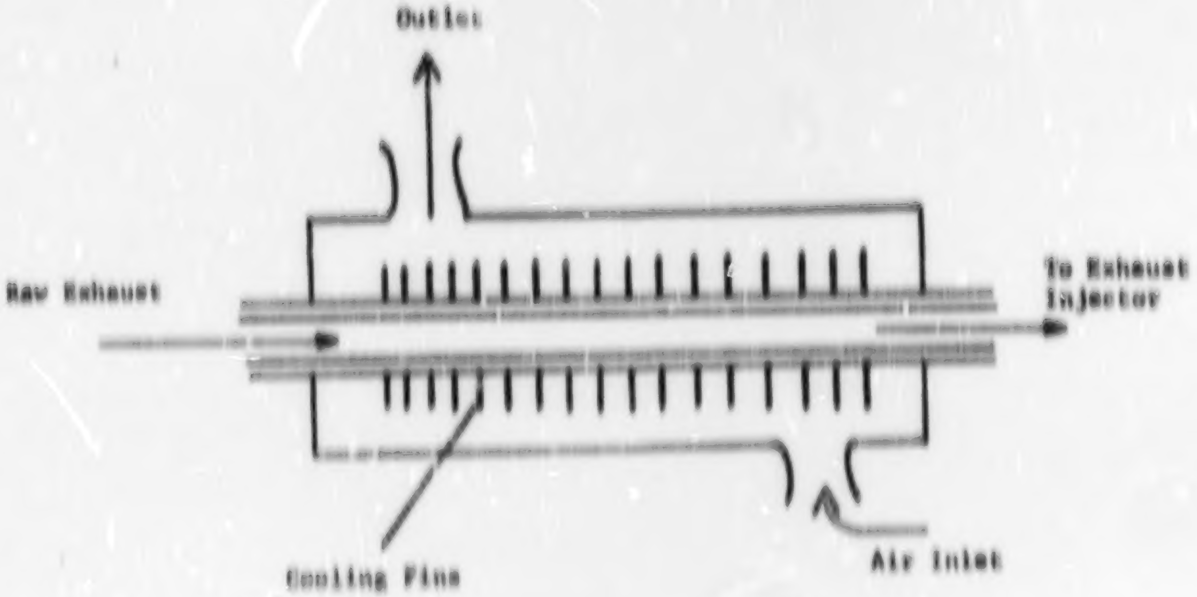


FIGURE C-8

FINNED TUBE COOLING SETUP



molecules energised to an excited state by the high intensity light source, return to the ground state by emitting a monochromatic light, which passes through a narrow-band filter, and impinges upon the light sensitive surface of a photomultiplier tube. The intensity of this radiation is directly proportional to the SO_2 concentration.

This measurement method was chosen because of the following reasons:

(1) It is more convenient than wet chemical, conductimetric, or coulometric methods.

(2) Both continuous and integrated measurements of SO_2 in diluted exhaust can be made.

(3) Measurement of SO_2 emission rates could be incorporated as part of the gaseous emission measurements routinely obtained using diluted exhaust collected by the CVS system.

The operating principle of the TECO analyser is depicted schematically in Figure C-9.

To eliminate the possibility of water adsorbing and condensing in the sample chamber on the walls and optical filters, the water in the sample stream was removed upstream to the TECO analyser. Initially, Drierite was used to remove the water, but it was found that at the 5 to 10 ppm level of SO_2, the Drierite removed all the SO_2.

The water removal problem was solved by using the Permatube Drying System (20) shown in Figure C-10. This system dries the sample stream by passing it through a bundle of tubes which are permeable to water but essentially impermeable to SO_2. Water is purged by counter-current flow of dry air or nitrogen. The effectiveness of the permeable system in reducing the water level of a humid sample stream below 10 ppm H_2O while retaining the SO_2 in the sample has been established by our Analytical Division. The Model PD-500-72 Perma Pure Dryer according to the manufacturer (20) has the capability of taking a feed having a 50°C dew point and extracting sufficient water at 150 litres/hr feed rate to reduce the dew point of the effluent to -30°C.

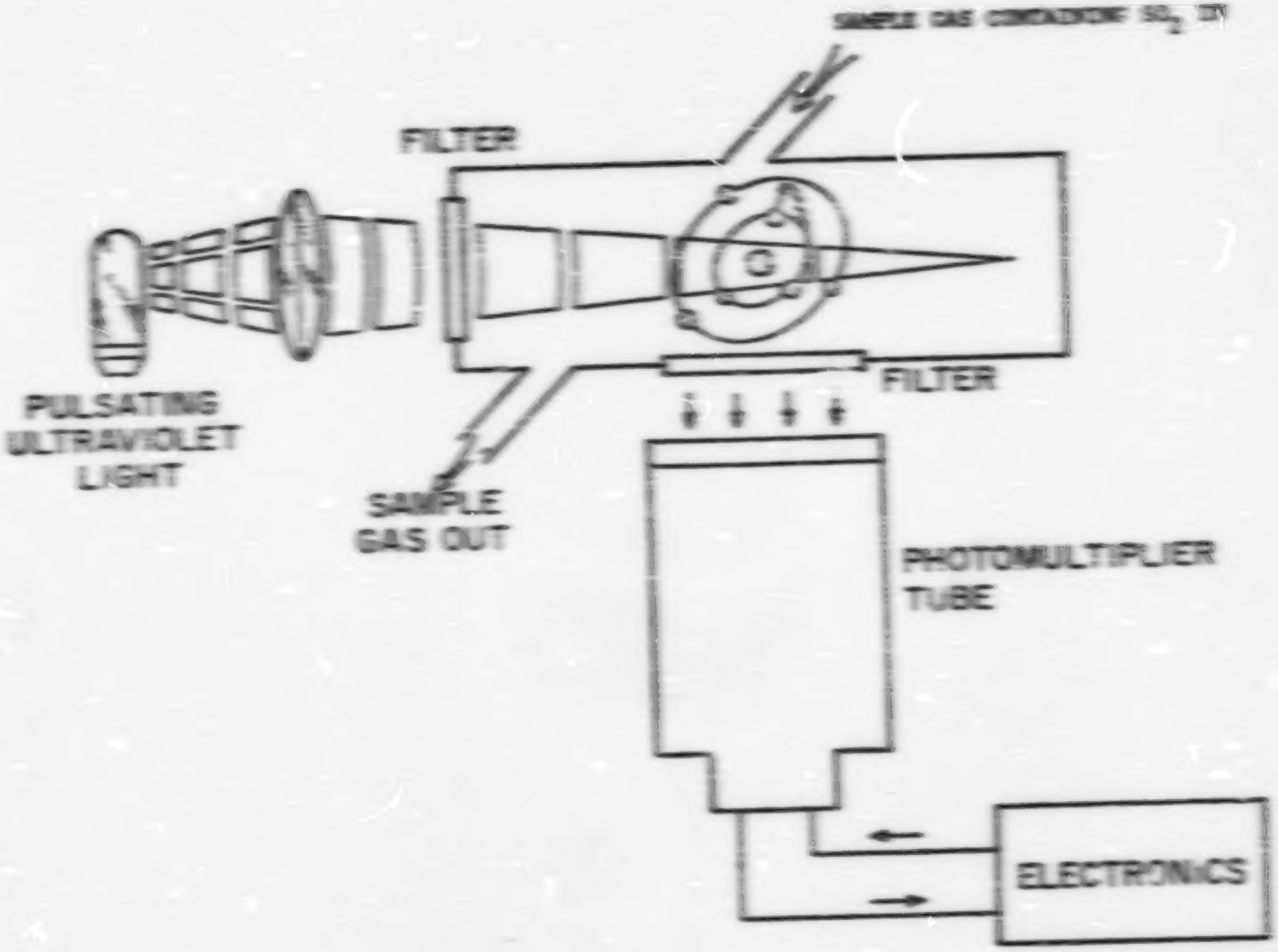
Our own tests with dry SO_2 in N_2 and in air have shown that no differences in TECO readings were obtained when the sample is introduced directly into the analyser, or what it passes through the dryer prior to entry into the analyser.

A millipore filter is used upstream to the dryer to prevent any particulate matter from entering and eventually clogging the dryer, and for that matter, from possibly entering and contaminating the analyser.

FIGURE C-9

PRINCIPAL OF OPERATION

TECO SO_2 INSTRUMENT



It has been found that CO_2, CO, and O_2 are strong quenching agents, while N_2 exhibits a negligible quenching effect. The instrument reponse is therefore sensitive to background gas composition. Absolute values of SO_2 concentrations necessitate calibration of the instrument in a background representative of the sample to be analyzed. For example, prior to a laboratory study on SO_2 conversion as a function of oxygen concentration, it was necessary to assess the effect of oxygen quenching (2). Various samples were made by preparing bell jar mixtures containing 30 ppm SO_2, 12% CO_2, varied amounts of oxygen, and nitrogen as the balance gas. Measurements of the SO_2 concentration of these mixtures indicate an approximate 1 ppm reduction in instrument SO_2 response for each 2% increment in oxygen concentration, as shown below.

Table C-1

SO_2 Measurements at Indicated Oxygen Concentrations(a)

Oxygen Concentration (%)	TECO SO_2 Response (ppm)
0	29.7
1	28.8
2	28.4
4	26.8
6	26.2

(a) Basis Mixture, 30 ppm SO_2, 12% CO_2, balance N_2.

The quenching effects of CO and CO_2 was also measured using mixtures of 30 ppm SO_2 in pure CO and CO_2. In CO_2, the response to 30 ppm of SO_2 was 1.7 ppm, that in CO only 0.5. Measurements were then carried out on bell jar mixtures of 30 ppm of SO_2 in background air containing different concentrations of CO, O_2, C_3H_8, and CO_2. The results given below show that instrument response is sensitive to overall concentration of quenching species. Therefore data obtained where the total background concentration of quenching species changes significantly from the calibration gas quencher level should be corrected for the inherent changes in instrument response.

Table C-3

Composite Effects of CO_2, O_2 and CO on TECO SO_2 Response

Mixture Composition	Total Quencher Species Concentration (%) $[CO_2] + [O_2] + [CO]$	Instrument Response (ppm)
30 ppm SO_2 1.42% O_2 0.07% CO 0.051% H_2 445 ppm C_3H_8 12.5% CO_2	14.0	28
30 ppm SO_2 4.78% O_2 14.3% CO_2 4.19% CO 348 ppm C_3H_8	23.4	23

For work with dilute exhaust, quenching effects are minor. Quenching by exhaust CO_2 and CO is negligible for a CVS air diluted sample due to dilution. Although the oxygen concentration increases with dilution, it presents a reasonably constant quench background and can be taken into account by calibration of dilute SO_2 in air mixtures. Properly used, the precision of this instrument is about 0.5 ppm SO_2.

C.5 Analytical Method for Determination of Sulfate on Glass Fiber Filters Using a Recording Titrator and Probe Colorimeter

The filters are extracted with water, and the resulting solution is passed through an ion exchange resin to remove cations. Sulfate is then titrated to the thorin endpoint using a recording titrator and probe colorimeter. Sulfate can be measured if it is present in solution in amounts of 10 ug or greater. The use of a recording titrator interfaced with a probe colorimeter to sense colorimetric endpoints is better suited to determination of low levels of sulfate than titration to a visual endpoint. The titration system automatically plots the volume of titrant dispensed from a driven burette against the change in color of the indicator.

Reagents

1. Barium perchlorate solution, 0.00521 M, available from Hach Chemical Company, Ames, Iowa.

2. Barium perchlorate solution, 0.000521 M in 80% 2-propanol prepared from the above solution. (Propanol, distilled in glass, is available from Burdick and Jackson Labs, Inc., Muskegon, Michigan.)

3. Thorin indicator, 0.2% in water. This indicator is available as a powder from the Hach Chemical Company.

4. Dowex 50W-X8 Cation Exchange Resin, 50-100 mesh.

5. Sulfuric acid solution 0.1000 N for standardizing the barium perchlorate solution. This solution is available from the Harleco Division of the American Hospital Supply Corporation, Gibbstown, New Jersey. As received, this acid solution is standardized to contain 4.90 g H_2SO_4 per litre at 25°C. The acid is standardized at Harleco against tris hydroxymethyl aminomethane using methyl red as the indicator.

Standardization of the Barium Perchlorate Titrant

The burette reservoir and burette are filled with 0.000521 M barium perchlorate solution. The electronic agreement of the PC/600 and the E536 titrator is checked as described in the manufacturer's instruction manual of operation. The instrumental parameters are set as indicated below:

- Burette speed = 10 min/100% volume
- Mode switch = pH/mv position
- Chart range = 1 pH full scale
- Chart speed = 400 mm/100% volume
- Temperature compensator - set at room temperature
- Colorimeter filter = 520 nm

The position of the probe in the titration vessel is situated so that the solution can be stirred through the probe without bubble formation, since this would result in an unstable baseline.

1. Pipet 5 ml of previously standardized 0.001 N H_2SO_4 into a 100 ml beaker equipped with a Teflon-coated magnetic stirring bar. This contains 0.005 meq H_2SO_4, (0.0025 m mol $SO_4^=$ 0.24 mg $SO_4^=$).

2. Add 5 ml of water and 40 ml of 2-propanol to the beaker.

3. Add 3 drops thorin indicator to the beaker.

4. Degas the solution by stirring for 3 min. on a magnetic stirrer.

5. Place the beaker on the titration stand and put the colorimeter probe and burette tip into the beaker.

6. Titrate the solution and determine the endpoint, as shown in Figure I, record the volume, V_A.

7. Calculate the sulfate equivalent of the barium perchlorate titrant, C, as follows:

$$C = \frac{\text{mg } SO_4^=}{\text{ml } Ba(ClO_4)_2 \text{ sol'n}} = \frac{0.24 \text{ mg } SO_4^=}{V_A \text{ ml } 0.000521 \text{ N } Ba(ClO_4)_2}$$

Instrumentation

Sulfate titrations are performed using a Brinkman Metrohm Herisau Potentiograph Recording Titrator. This system automatically plots the volume of titrant dispensed versus the color of the indicator.

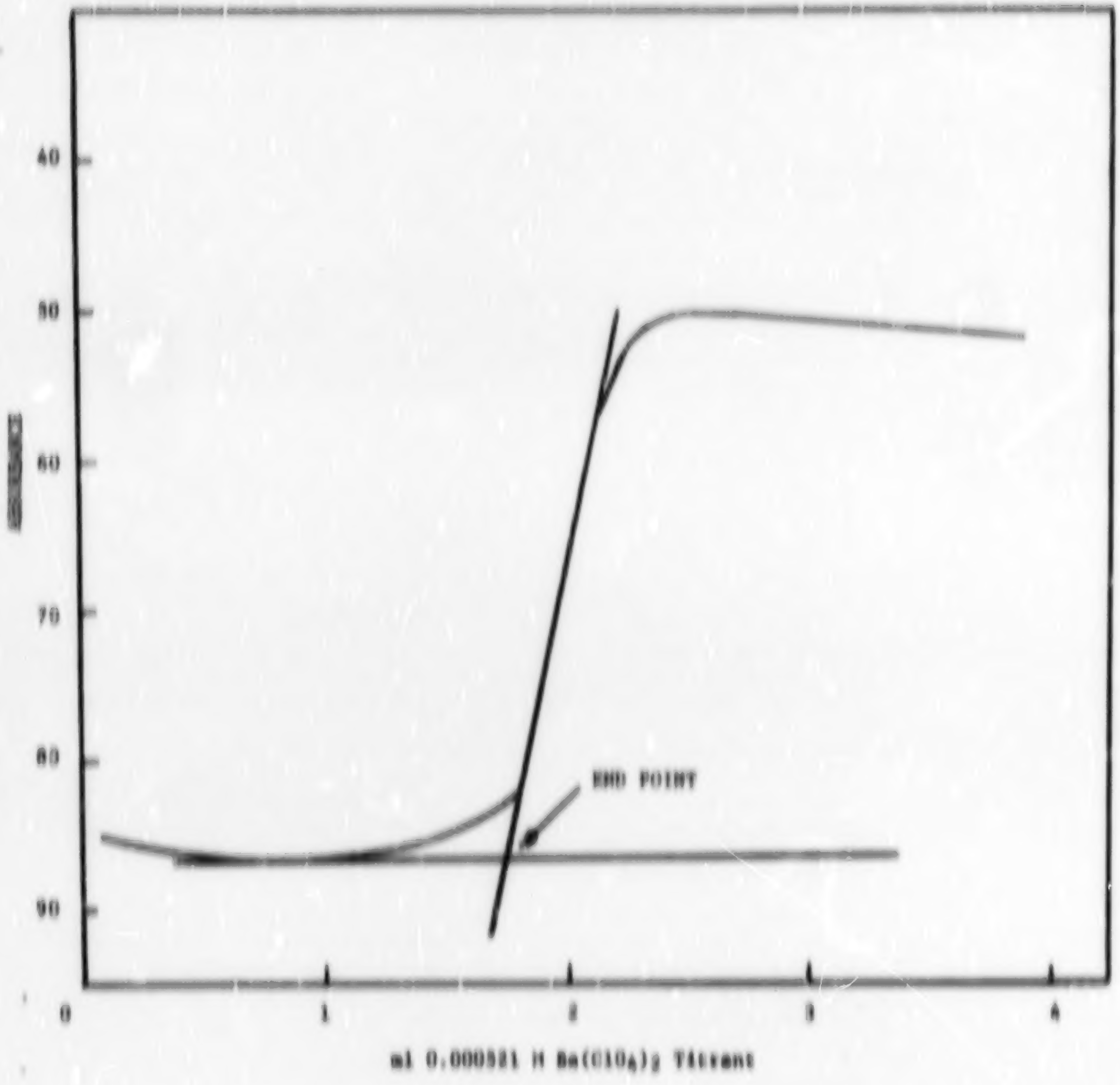
This titration system consists of the following components:

- E536 titrator
- E535/4 titration stand
- E522-10S, 10 ml burette
- Brinkman Probe Colorimeter (PC600 colorimeter)

The recorder output of the PC600, 100 mv, is directly related to the 100 mv range of the E536 titrator. The chart drive of the recorder is synchronized with the burette drive. Burette run-out times can be varied from 5 to 300 minutes corresponding to chart speeds of 60 to 2mm per minute.

FIGURE C-10

TITRATION OF SULFATE USING THORIN INDICATOR



The Brinkman Probe Colorimeter consists of a PC600 colorimeter, a 2 cm light path stainless steel fiber optics probe and 520 or 650 nm interference filters. The filter colorimeter employs a fiber optics probe which is placed in the solution to be titrated. Phase shifted AC amplified light is transmitted to the probe to avoid interference from ambient light.

The entire titrator assembly is available from Brinkman Instruments, Westbury, New York.. A detailed description of the titrator-colorimeter system is contained in the manufacturers' instruction manuals of operation (Instructions for Use E536 Metrohm AG CH-9100 Herisau and Operating Instructions for the Brinkman PC600 Probe Colorimeter). Figure C-12 shows a block diagram of the colorimeter and the photometric probe.

Stepwise Procedure of Work-Up of Sulfate-Containing Glass Fiber Particulate Filters

1. The filter to be analyzed is cut into quarters with an exacto knife using a right angle lucite template placed on the filter as a guide. No part of the template actually touches the part of the filter to be analyzed.

2. The filter quarter section is folded, put into a 100 ml beaker, and covered with 25 ml of doubly distilled deionized water. Care is taken to ascertain that the whole filter is wet and covered with water.

3. The beaker is covered with a watch glass and glass stirring rod inserted between the beaker and watch glass.

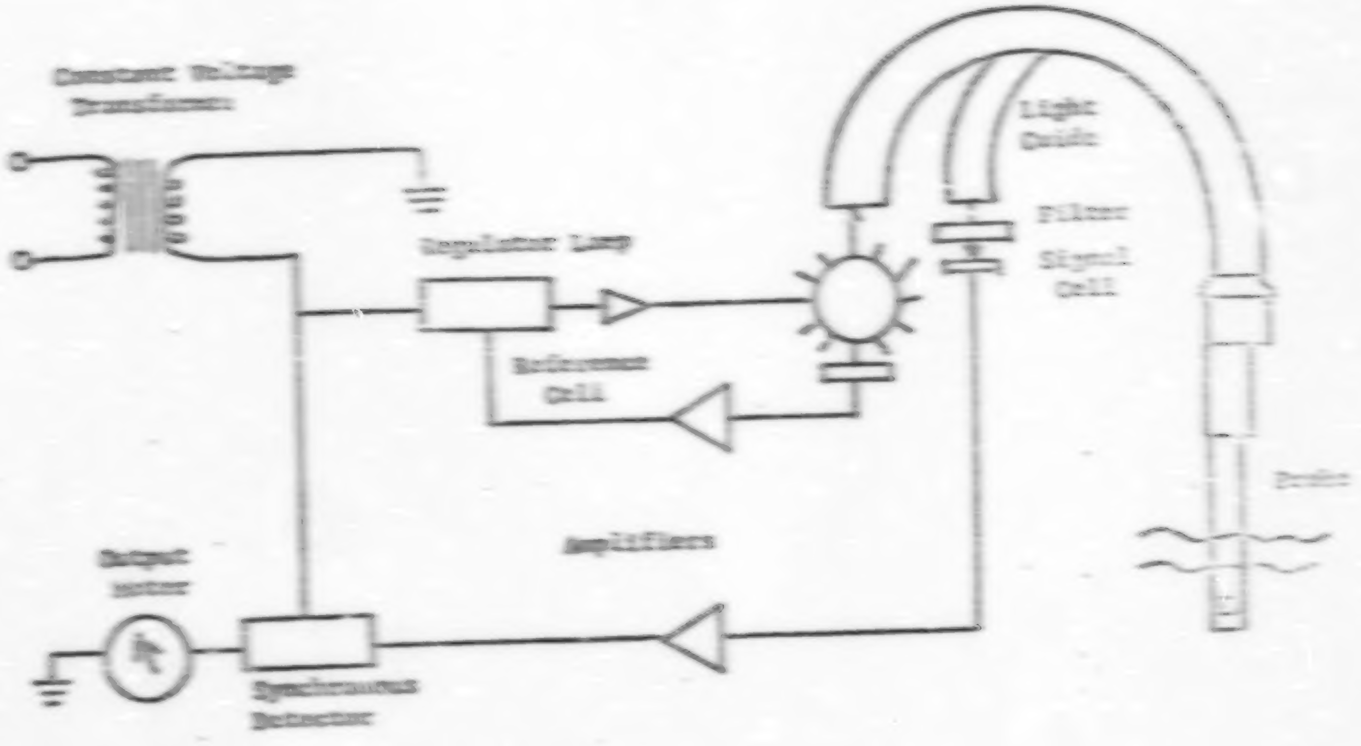
4. The sample is digested by placing the beaker on a hot plate (set low) and allowed to boil for 5 minutes. Following digestion, the sample is allowed to cool down to room temperature.

5. The supernatant is filtered either through fine glass wool (Pyrex Brand Wool, Corning Glass Works) or a paper filter (9 cm diameter, Schleicher and Schuell, Inc.) into an ion-exchange column (1 cm x 25 cm) containing about 7.5 ± 0.5 inches of Dowex 50 WX8 cation exchange resin, collecting the sample in a 50 ml volumetric flask.

6. The beaker is washed three times with 5 ml portions of distilled deionized water, the washings added to the column. After each washing, liquid is squeezed from the filter by pressing it against the wall of the beaker with the stirring rod and added to the column with the wash solution.

FIGURE C-11

BLOCK DIAGRAM OF [illegible] [illegible] PROBE COLORIMETER



7. The volume of liquid in the volumetric flask is made up to the mark by the addition of distilled, deionized water. This solution is the basic filter leach solution from which the sulfate content of the filter and ultimately the vehicle sulfate emission rate is determined.

Titration of Filter Leach Solution for Sulfate

1. A suitable aliquot, V_S, is added to a 100 ml beaker, containing a magnetic stirring bar.

2. Sufficient water is added to the beaker so that the total volume (aliquot plus added water) equals 10 ml.

3. 40 ml of 2-propanol and 3 drops of the thorin solution are added to the beaker.

4. The solution is degassed by stirring for 5 minutes with a magnetic stirrer.

5. The solution is titrated using the Brinkman titrator to determine the endpoint with V_C ml of titrant, recording the titrant volume. The endpoint is determined from the absorbance versus volume of titrant chart as shown in Figure C-11.

In the process of developing this analytical procedure, the following precautionary steps were found to be necessary:

1. Insure that sufficient column capacity remains to remove the metals in the sample. Use a new Dowex column on each high level sample. Dowex can't be regenerated with HCl since results show a carry-over.

2. Insure that at least 1 ml of the titrant is consumed in the titration. If less than 1 ml is consumed, place a 20 ml aliquot of the sample in a 150 ml beaker, add 80 ml of 2-propanol and add a known quantity of sulfuric acid sufficient to give a titration of 1 to 3 ml. Titrate the solution. Calculate as outlined below and subtract the known mg $SO_4^=$ added to give the mg $SO_4^=$ in the filter.

$$\frac{\text{mg } SO_4^=}{\text{Filter}} = (V_C \text{ ml } Ba(ClO_4)_2 \text{ soln}) \times \frac{C \text{ mg } SO_4^=}{\text{ml } Ba(ClO_4)_2 \text{ soln}} \times \underbrace{\frac{50 \text{ ml}}{V_S \text{ ml}}}_{\substack{\text{aliquot}\\ \text{factor}}} \times \underbrace{\frac{4}{1 \text{ Filter}}}_{\substack{\text{filter}\\ \text{factor}}}$$

Additional Procedural Changes

To demonstrate that water and nitric acid remove equivalent amounts of sulfate from the filters, comparison extraction data was obtained. One quadrant of fiber glass filters from vehicle tests was extracted with dilute nitric acid, the metals were removed by a cation exchange resin and the sulfate content was determined by the Sulfanazo III procedure. Another quadrant of the filters was extracted with water, the metals were removed by a cation exchange resin and the sulfate content was determined by the thorin procedure.

The results which were obtained are given in Table C-3 and indicate the extraction procedures are equivalent. On the basis of these results, it was decided to utilize the instrumental technique because of its inherent greater sensitivity and precision, coupled with thorin as the indicator.

When the visual titrimetric procedure for sulfate was supplanted by the automatic titrimetric method, the indicator used was also changed from Sulfanazo III to Thorin, to simplify the procedure. This indicator substitution necessitated the use of a water extraction of the filters in place of the original nitric acid extraction.

TABLE C-3

SULFATE EXTRACTIONS USING DILUTE NITRIC ACID AND WATER - COMPARISON DATA

Filter #, AL	mg $SO_4^=$/Filter H_2O Extraction	 HNO_3 Extraction	%Δ (HNO_3 - H_2O)
708631	27.21	28.28	+ 3.8
32	26.13	29.09	+10.3
33	1.09	0.90	-22.2
34	0.84	1.11	+33.4
35	1.06	1.04	- 1.9
36	1.25	1.25	0.0
37	1.25	1.49	-16.1
38	1.19	1.65	+37.9
39	0.81	0.99	+18.2
40	0.95	1.00	+ 4.0
708617	3.68	3.38	- 8.9
18	2.59	2.51	- 3.2
19	2.66	2.73	+ 2.3
20	3.63	3.50	- 3.4
21	4.31	4.22	- 2.4
22	2.30	2.36	+ 2.5
23	2.21	2.30	+ 3.5
24	0.25	0.15	-40.0
25	3.96	3.13	-26.5
26	3.49	3.03	-15.2
27	3.14	2.69	-17.1
28	2.15	2.33	+ 1.1
		Average	- 2.3

APPENDIX D

TABLE D-1

TEST CAR 124 - $SO_4^=$ TRAP VEHICLE[1]
CONTAINING BENCHMARK RINGS (12.7 mm ID)

(Fuel Sulfur, 320 ppm)

Kilometers	Test Sequence	Exhaust Gas Emissions					$SO_4^=$ Trapping Efficiency, %
		CO	HC	NO_x	SO_2	$SO_4^=$	
		g/km			mg/km		
0, No Trap (Base Case)	FTP	1.98	0.18	4.26	48.6	7.7	
	SET	0.67	0.14	7.82	91.5	10.8	
	SET	1.05	0.15	7.78	80.2	5.1	
	FET	0.26	0.12	9.46	44.8	10.9	
	SET	0.95	0.12	8.13	90.5	6.2	
	SET	0.87	0.12	7.94	72.1	3.7	
0, No Trap (Base Case)	FTP	3.38	0.20	5.53	42.7	5.5	
	SET	1.24	0.11	8.09	99.3	4.9	
	SET	0.71	0.10	7.94	64.9	4.1	
	FET	0.25	0.12	10.19	47.2	10.7	
	SET	2.07	0.27	7.41	72.6	4.8	
	SET	0.50	0.10	8.34	93.8	8.5	
0, With Trap	FTP	2.92	0.31	5.73	43.1	4.3	34.8
	SET	0.57	0.22	7.71	26.6	3.5	40.0
	SET	0.90	0.11	7.80	32.6	2.7	40.0
	FET	0.38	0.11	9.68	40.6	1.8	83.3
	SET	0.48	0.12	8.45	27.8	2.4	60.0
	SET	0.99	0.13	7.53	42.2	2.1	65.0
0, With Trap	FTP	2.76	0.26	5.86	21.9	5.1	22.7
	SET	0.53	0.11	8.25	34.1	3.4	43.3
	SET	—	—	—	38.5	2.8	53.3
	FET	0.26	0.27	9.95	29.0	4.5	58.3
	SET	0.65	0.21	8.31	51.8	3.1	48.3
	SET	—	—	—	31.4	3.2	46.7

(1) 1974 car equipped with PTX-IIB oxidation catalysts and air pump.

TABLE D-1 (CONTINUED)

Kilometres	Test Sequence	Exhaust Gas Emissions					$SO_4^=$ Trapping Efficiency, %
		CO	HC	NO_x	SO_2	$SO_4^=$	
		g/km			mg/km		
6 400, With Trap	FTP	2.82	0.12	3.27	41.8	12.0	0
	SET	0.31	0.08	5.07	50.3	5.4	30.0
	SET	0.55	0.09	5.23	50.5	3.6	40.0
	FET	0.11	0.04	4.78	14.3	8.0	25.9
	SET	0.80	0.28	4.83	50.4	4.4	26.7
	SET	0.78	0.21	4.51	50.6	4.2	30.0
	96 km/h	0.04	0.04	8.01	37.7	25.0	——
	64 km/h	0.02	0.02	3.10	6.1	29.5	——
16 000, With Trap	FTP	1.39	0.25	4.38	28.4	7.3	0
	SET	0.46	0.18	5.07	58.5	5.1	52.4
16 000, No Trap	FTP	3.03	0.41	5.27	85.5	6.4	
	SET	0.36	0.34	5.95	72.3	10.5	

APPENDIX D

TABLE D-2

TEST CAR 124[1] - SO$_4^=$ TRAP VEHICLE CONTAINING BENCHMARK PELLETS (4.76 mm OD)*[2]

(Fuel Sulfur, 320 ppm)

Kilometres	Test Sequence	CO	HC	NO$_x$	SO$_2$	SO$_4^=$	SO$_4^=$ Trapping Efficiency, %
		g/km			mg/km		
0, No Trap (Base Case)	FTP	1.97	0.29	7.26	63.0	4.1	
	SET	0.48	0.14	6.68	5.1	6.6	
	SET	0.37	0.13	3.78	5.1	8.0	
	FET	0.48	0.18	4.61	51.9	10.6	
	SET	0.35	0.12	5.91	5.1	9.6	
	SET	0.49	0.15	6.35	60.8	12.1	
	96 km/h (2 hours)	0.07	0.08	10.67	46.6	25.9	
0, With Trap	FTP	1.95	0.20	5.90	6.0	2.7	34.1
	SET	0.36	0.15	5.15	5.0	0.5	94.3
	SET	0.43	0.13	5.56	5.0	0.5	94.3
	FET	0.40	0.20	6.37	6.5	0.3	97.2
	SET	0.46	0.12	4.91	5.2	0.4	95.5
	SET	0.44	0.15	5.05	5.2	0.2	97.7
	96 km/h (2 hours)	0.07	0.08	8.91	2.3	0.4	98.5
5 000, With Trap	FTP	2.11	0.27	4.04	40.1	2.9	29.0
	SET	0.22	0.09	4.95	41.7	0.9	88.6
	SET	0.43	0.10	5.12	45.6	1.1	87.5
	FET	0.27	0.11	5.80	28.7	0.8	92.5
	SET	0.81	0.11	4.38	40.3	0.8	90.9
	SET	0.45	0.15	4.72	47.0	0.7	92.0
	96 km/h (2 hours)	0.05	0.07	5.76	10.1	0.5	98.1

(1) Test Car 124 - 1974 car equipped with two PTX-IIB catalysts and air pump.
(2) No trap where noted.

TABLE D-2 (CONTINUED)

Kilometres	Test Sequence	CO	HC	NO_x	SO_2	$SO_4^=$	$SO_4^=$ Trapping Efficiency, % I(1)	$SO_4^=$ Trapping Efficiency, % II(2)
		g/km			mg/km			
15 000, with trap	FTP	2.03	0.27	3.77	72.5	4.1	0	0
	SET	0.46	0.11	3.87	68.0	2.0	77.3	0
	SET	0.42	0.13	3.78	54.0	1.9	79.5	14.3
	FET	1.74	0.17	3.57	63.2	1.5	85.0	28.6
	SET	0.57	0.11	3.33	64.5	1.5	83.0	73.2
	SET	0.88	0.11	3.26	68.0	2.0	77.3	4.8
	96 km/h (2 hours)	0.29	0.12	4.82	30.0	3.0	88.4	83.9
15 000, no trap (Base Case)	FTP	2.31	0.37	3.45	6.5	3.0		
	SET	0.71	0.14	4.36	82.1	2.1		
	FET	0.51	0.16	5.93	37.4	5.6		
	96 km/h (1 hour)	0.20	0.08	7.29	59.0	18.7		

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(1) % efficiency calculated using 0 km no trap $SO_4^=$ levels.
(2) % efficiency calculated using 15 000 km no trap $SO_4^=$ levels.

APPENDIX D

TABLE D-3

TEST CAR 99(1) - $SO_4^=$ TRAP VEHICLE CONTAINING $Ca(OH)_2$/DICALITE (4.76 mm PELLETS)

(Fuel Sulfur, 320 ppm)

Kilometres	Test Sequence	Exhaust Gas Emissions CO	HC	NO_x	SO_2	$SO_4^=$	$SO_4^=$ Trapping Efficiency, %
		------ g/km	------	------	--- mg/km	---	
0, No Trap (Base Case)	FTP	1.11	0.14	2.30	10.9	4.5	
	SET	0.34	0.08	2.58	35.0	29.5	
	SET	0.23	0.06	2.69	33.2	31.6	
	FET	0.33	0.06	2.80	32.9	35.4	
	SET	0.55	0.10	2.60	34.8	42.0	
	SET	0.45	0.13	2.64	30.8	50.4	
	96 km/h (2 hours)	0.16	0.05	2.25	25.8	51.7	
0, With Trap	FTP	0.91	0.14	2.34	25.9	1.5	65.6
	SET	0.29	0.06	2.39	9.5	0.6	98.0
	SET	0.42	0.11	2.34	6.0	0.6	98.4
	FET	1.54	0.11	2.50	7.9	0.8	97.7
	SET	0.82	0.09	2.40	17.8	1.3	96.6
	SET	0.53	0.14	2.55	10.6	1.8	95.3
	96 km/h (2 hours)	0.31	0.03	2.30	27.8	5.7	89.0
5 000, With Trap	FTP	2.19	0.25	2.42	40.9	37.8	0
	SET	0.62	0.09	2.67	31.1	24.3	49.7
	SET	0.59	0.12	2.67	30.2	15.7	39.1
	FET	2.91	0.09	2.64	27.9	12.3	65.3
	SET	0.69	0.08	2.27	30.4	15.7	59.1
	SET	1.53	0.09	2.38	21.9	15.0	60.9
	96 km/h (2 hours)	0.36	0.04	3.03	26.8	20.6	60.2
15 000, With Trap	FTP	2.50	0.49	2.71	61.4	12.7	0
	SET	0.75	0.17	3.30	46.5	13.0	66.1
	SET	0.70	0.14	3.21	30.3	15.0	60.9
	FET	2.95	0.16	3.72	33.3	13.4	62.1
	SET	0.98	0.14	2.70	44.9	18.1	52.8
	SET	1.11	0.18	2.86	46.6	17.8	53.6
	96 km/h (2 hours)	0.58	0.05	3.30	45.3	19.4	62.5

(1) Test Car 99 - 1972 car with two PTX-423 oxidation catalysts and an air pump.

APPENDIX B

TABLE B-1

1975 VEHICLE (351 CID)
Pt/Pd OXIDATION CATALYSTS (AEW 3/60/500)

(Fuel Sulfur = 0.032 Wt %)

Kilometres	1975 FTP, g/km					% Fuel Sulfur As	
	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	2.62	0.78	1.67	0.023	0.009	30.6	5.5
3 200	2.45	0.29	1.64	0.059	0.011	54.9	8.1
6 400	3.39	0.39	1.61	0.085	0.009	79.5	5.6
9 600	2.93	0.43	1.70	0.071	0.013	67.4	9.0
12 800	2.48	0.28	1.84	0.086	0.014	86.4	9.4

Kilometres	FET, g/km					% Fuel Sulfur As	
	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	0.12	0.06	2.66	0.019	0.024	27.2	22.3
3 200	0.11	0.14	2.16	0.034	0.028	50.0	27.4
6 400	0.36	0.14	2.06	0.026	0.034	38.3	33.5
9 600	0.19	0.07	2.46	0.035	0.042	52.1	41.6
12 800	0.29	0.09	2.73	0.034	0.055	53.4	57.2

Kilometres	SET, g/km					% Fuel Sulfur As	
	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	0.40	0.11	2.37	0.033	0.028	42.7	23.7
3 200	0.77	0.09	3.23	0.068	0.022	85.1	16.5
6 400	0.94	0.12	2.00	0.046	0.033	58.8	28.5
9 600	0.26	0.07	2.30	0.045	0.018	60.7	15.7
12 800	0.98	0.12	2.29	0.056	0.026	80.5	25.1

(a) SO_2 = bubbler method

(b) $SO_4^=$ = particulate filter

APPENDIX B

TABLE B-1 (Cont.)

	Idle, g/Test					% Fuel Sulfur As	
Kilometres	CO	HC	NO_x	SO_2(a)	$SO_4^=$(b)	SO_2	$SO_4^=$
0	0.21	0.68	2.63	0.112	0.009	17.1	1.0
3 200	0.22	0.77	2.17	0.115	0.001	17.6	0.1
6 400	0.94	0.12	2.00	0.117	0.015	18.1	1.6
9 600	0.46	0.99	2.24	0.117	0.015	19.2	1.6
12 800	0.20	0.61	2.12	0.114	0.018	20.7	2.2

		64 km/h, g/km					% Fuel Sulfur As	
Kilometres		CO	HC	NO_x	SO_2(a)	$SO_4^=$(b)	SO_2	$SO_4^=$
0	I	0.04	0.02	0.58	0.021(c)	0.064(d)	30.8	62.1
	II	0.04	0.02	0.52		0.057		56.5
3 200	I	0.07	0.02	0.65	0.029	0.055	41.9	52.8
	II	0.06	0.02	0.58		0.054		51.6
6 400	I	0.05	0.02	0.66	0.024	0.058	34.2	55.0
	II	0.05	0.02	0.62		0.054		51.2
9 600	I	0.08	0.03	0.70	0.025	0.058	37.4	57.5
	II	0.07	0.03	0.73		0.057		56.5
12 800	I	0.06	0.02	0.67	0.024	0.061	38.3	66.4
	II	0.06	0.02	0.69		0.059		62.6

		96 km/h, g/km					% Fuel Sulfur As	
Kilometres		CO	HC	NO_x	SO_2(a)	$SO_4^=$(b)	SO_2	$SO_4^=$
0	I	0.06	0.02	3.34	0.029(c)	0.063(d)	43.8	64.2
	II	0.05	0.02	3.40		0.053		53.8
3 200	I	0.08	0.02	2.65	0.030	0.055	74.2	56.3
	II	0.11	0.02	2.53		0.049		47.6
6 400	I	0.09	0.03	3.37	0.040	0.064	59.1	62.3
	II	0.09	0.02	3.29		0.050		67.8
9 600	I	0.09	0.03	4.16	0.037	0.059	56.4	59.5
	II	0.10	0.03	4.42		0.053		49.9
12 800	I	0.09	0.04	3.76	0.036	0.062	58.7	68.1
	II	0.09	0.04	3.81		0.052		57.8

(a) SO_2 = bubbler method

(b) $SO_4^=$ = particulate filter

(c) One sample taken over the 1 hour test

(d) One sample taken for 20 minutes during each half hour segment

APPENDIX B

TABLE B-2

1975 VEHICLE (351 CID)
Pt/Rh OXIDATION CATALYSTS (ARV 2/3C/40/H)

(Fuel Sulfur = 0.032 Wt %)

	1975 FTP, g/km					% Fuel Sulfur As	
Kilometres	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	3.98(c)	0.62	1.70	0.066	0.004	51.3	1.9
3 200	2.38(c)	0.28	1.66	0.050	0.005	40.3	2.6
6 400	3.40(c)	0.28	1.70	0.115	0.003	92.2	2.7
9 600	2.61(c)	0.26	1.77	0.058	0.009	48.5	5.0
12 800	2.90(c)	0.42	1.57	0.118	0.007	93.7	3.7

	FET, g/km					% Fuel Sulfur As	
Kilometres	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	0.13	0.04	3.03	0.058	0.005	45.6	4.3
3 200	0.26	0.05	2.73	0.028	0.023	31.0	17.7
6 400	0.24	0.04	2.36	0.060	0.028	51.3	23.9
9 600	0.21	0.05	2.85	0.038	0.029	45.0	26.0
12 800	0.32	0.05	2.73	0.038	0.020	68.5	16.2

	SET, g/km					% Fuel Sulfur As	
Kilometres	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	1.33	0.04	2.27	0.081	0.004	86.5	2.7
3 200	1.61	0.05	2.42	0.084	0.008	102.2	6.1
6 400	1.13	0.04	2.52	0.083	0.012	92.2	8.8
9 600	0.85	0.05	2.63	0.053	0.017	61.2	13.2
12 800	0.98	0.08	2.67	0.085	0.009	88.5	6.2

(a) SO_2 = bubbler method
(b) $SO_4^=$ = particulate-filter
(c) One to two stalls on cold start

APPENDIX E

TABLE 1 (Cont.)

Kilometres	Idle, g/test CO	 HC	 NO_x	 SO_2 (a)	 $SO_4^=$ (b)	% Fuel Sulfur As SO_2	 $SO_4^=$
0	0.81	0.57	0.61	0	0	0	0
3 200	0.06	0.29	2.38	0	0.013	0	1.3
6 400	0.27	0.30	2.16	0.107	0.008	16.6	0.8
9 600	0.06	0.43	2.33	0	0.009	0	0.9
12 800	0.15	0.51	1.88	0	0.017	0	1.7

Kilometres		64 km/h, g/km CO	 HC	 NO_x	 SO_2 (a)	 $SO_4^=$ (b)	% Fuel Sulfur As SO_2	 $SO_4^=$
0	I	0.10	0.03	0.96	0.0174(c)	0.008(d)	21.8	6.6
	II	0.06	0.02	0.87		0.021		17.8
3 200	I	0.09	--	0.84	0.0267	0.026	34.2	21.9
	II	0.07	--	0.78		0.036		30.7
6 400	I	0.10	0.02	0.77	0.038	0.025	48.1	21.2
	II	0.11	0.01	0.74		0.028		23.7
9 600	I	0.12	0.01	0.71	0.038	0.026	48.0	22.3
	II	0.12	0.01	0.63		0.026		22.8
12 800	I	0.17	0.02	0.83	0.044	0.024	55.3	20.0
	II	0.14	0.02	0.76		0.023		19.4

Kilometres		96 km/h, g/km CO	 HC	 NO_x	 SO_2 (a)	 $SO_4^=$ (b)	% Fuel Sulfur As SO_2	 $SO_4^=$
0	I	0.10	0.04	5.08	0.048(c)	0.035(d)	56.8	37.4
	II	0.09	0.04	5.26		0.027		20.7
3 200	I	0.13	0.02	6.49	0.060	0.047	69.5	36.3
	II	0.12	0.02	6.77		0.032		26.1
6 400	I	0.16	0.02	5.79	0.056	0.035	66.2	27.5
	II	0.16	0.02	6.05		0.027		20.7
9 600	I	0.19	0.03	6.49	0.056	0.039	68.8	31.7
	II	0.19	0.03	6.58		0.027		21.9
12 800	I	0.28	0.03	7.76	0.071	0.039	77.6	28.3
	II	0.36	0.03	8.12		0.022		15.3

(a) SO_2 - bubbler method
(b) $SO_4^=$ - particulate-filter
(c) One sample taken over the 1 hour test
(d) One sample taken for 20 minutes during each half hour segment

APPENDIX E

TABLE E-3

1975 VEHICLE (351 CID)
Pt OXIDATION CATALYSTS (ABW 3/12C/40/M)

(Fuel Sulfur = 0.032 Wt %)

	1975 FTP, g/km					% Fuel Sulfur As	
Kilometres	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	2.38	0.36	1.89	0.087	0.[illegible]	85.2	3.6
3 200	1.79	0.26	1.59	0.056	0.011	52.4	7.1
6 400	1.95	0.26	1.76	0.058	0.016	52.3	9.5
9 600	2.33	0.34	1.87	0.042	0.017	38.6	10.2
12 800	2.96	0.43	1.81	0.069	0.021	63.1	13.0

	FET, g/km					% Fuel Sulfur As	
Kilometres	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	0.16	0.03	2.62	0.067	0.009	86.4	7.6
3 200	0.72	0.10	2.81	0.033	0.033	43.2	29.3
6 400	0.38	0.05	2.29	0.033	0.038	47.5	36.1
9 600	0.82	0.11	2.50	0.028	0.040	40.5	39.3
12 800	0.51	0.10	2.70	0.045	0.064	65.2	62.1

	SET, g/km					% Fuel Sulfur As	
Kilometres	CO	HC	NO_x	SO_2 (a)	$SO_4^=$ (b)	SO_2	$SO_4^=$
0	0.46	0.05	2.39	0.064	0.010	77.5	8.0
3 200	0.56	0.12	2.57	0.032	0.057	38.3	29.9
6 400	0.53	0.11	2.36	0.060	0.029	75.6	24.3
9 600	0.27	0.11	2.40	0.043	0.043	54.7	35.7
12 800	0.70	0.08	2.45	0.074	0.031	91.4	26.0

(a) SO_2 = bubbler method
(b) $SO_4^=$ = particulate filter

APPENDIX E

TABLE E-3 (cont.)

Kilometres	Idle, g/test					% Fuel Sulfur As	
	CO	HC	NO_x	$SO_2^{(a)}$	$SO_4^{=(b)}$	SO_2	$SO_4^{=}$
0	0.41	0.19	1.94	0.371	0.019	53.6	1.8
3 200	0.21	0.70	2.47	0.117	0.028	18.3	2.9
6 400	0.20	0.55	2.52	0.112	0.021	17.0	2.2
9 600	0.21	1.10	1.38	0.110	0.016	17.8	1.7
12 800	0.38	0.76	1.68	0.113	0.018	18.8	2.0

Kilometres		64 km/h, g/km					% Fuel Sulfur As	
		CO	HC	NO_x	$SO_2^{(a)}$	$SO_4^{=(b)}$	SO_2	$SO_4^{=}$
0	I	0.06	0.01	0.68	0.030(c)	0.036(d)	32.8	31.1
	II	0.06	0.01	0.68		0.043		37.3
3 200	I	0.05	0.02	0.59	0.034	0.061	49.5	38.0
	II	0.05	0.01	0.45		0.043		42.1
6 400	I	0.04	0.02	0.61	0.022	0.51	31.3	49.0
	II	0.05	0.03	0.57		0.52		49.9
9 600	I	0.08	0.03	0.72	0.023	0.059	31.6	55.8
	II	0.07	0.03	0.66		0.060		57.2
12 800	I	0.06	0.02	0.67	0.028	0.059	37.9	56.8
	II	0.06	0.02	0.66		0.055		51.8

Kilometres		96 km/h, g/km					% Fuel Sulfur As	
		CO	HC	NO_x	$SO_2^{(a)}$	$SO_4^{=(b)}$	SO_2	$SO_4^{=}$
0	I	0.06	0.01	4.74	.064(c)	0.038(d)	79.9	31.3
	II	0.06	0.03	4.74		0.31		25.3
3 200	I	0.06	0.02	4.72	.038	0.036	51.5	31.4
	II	0.06	0.03	4.28		0.046		41.1
6 400	I	0.05	0.03	4.21	.036	0.067	47.9	56.6
	II	0.07	0.03	4.46		0.059		55.0
9 600	I	0.05	0.03	3.65	.029	0.069	43.4	68.1
	II	0.05	0.02	3.59		0.057		55.4
12 800	I	0.08	0.02	3.91	.051	0.065	72.6	68.9
	II	0.11	0.02	3.66		0.047		45.2

(a) SO_2 = bubbler method
(b) $SO_4^{=}$ = particulate-filter
(c) One sample taken over the 1 hour test
(d) One sample taken for 20 minutes during each half hour segment

APPENDIX F

TABLE F-1

FUEL CONSUMPTION, (g/km)
1975 CAR, Pt-Pd (G-C) OXIDATION CATALYSTS

Kilometres		FTP	FET	SET	Idle[a]	64 km/h I	64 km/h II	96 km/h I	96 km/h II
0	Weight	170.0	104.1	119.6	885.3	104.2		101.6	
	Carbon Balance	171.3	110.6	121.9	1026.0	107.0	104.9	102.1	102.5
3 200	Weight	172.9	109.0	125.4	858.1	111.5		106.0	
	Carbon Balance	167.0	104.7	124.6	1021.5	108.7	108.1	105.4	107.0
6 400	Weight	169.8	104.4	123.6	921.6	109.1		108.3	
	Carbon Balance	167.2	105.2	121.3	976.1	109.8	109.8	106.8	108.3
9 600	Weight	167.8	107.9	116.7	858.1	109.5		108.9	
	Carbon Balance	164.7	104.9	116.5	948.9	104.9	104.9	103.8	110.7
12 800	Weight	176.0	111.7	124.0	866.4	110.7		112.3	
	Carbon Balance	155.4	108.8	108.8	858.1	97.1	98.2	94.6	93.7

(a) Fuel consumption at idle is reported in grams/test.

APPENDIX F

TABLE F-2

FUEL CONSUMPTION, (g/km)
1975 CaR, Pt-Rh (3-C) OXIDATION CATALYSTS

Kilometres		FTP	HET	SET	Idle[1]	64 km/h I	64 km/h II	96 km/h I	96 km/h II
0	Fuel Weight	177.5	119.9	130.8	549.3	113.7		130.1	
	Carbon Balance	185.1	121.8	136.4	626.5	116.6	117.4	124.1	129.8
3 200	Fuel Weight	176.5	124.2	132.5	908.8	112.7		126.6	
	Carbon Balance	181.9	126.4	133.9	1017.6	114.8	114.7	127.8	137.5
6 400	Fuel Weight	185.4	115.3	129.1	850.1	111.5		125.2	
	Carbon Balance	178.3	111.7	118.8	998.8	113.8	115.1	123.7	127.8
9 600	Fuel Weight	171.3	115.3	127.3	838.8	111.1		126.8	
	Carbon Balance	174.7	115.3	126.8	1021.5	114.3	111.7	128.9	127.2
12 800	Fuel Weight	183.7	115.3	137.8	876.2	114.6		130.6	
	Carbon Balance	184.7	118.5	141.4	998.8	117.5	115.9	135.7	141.2

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(1) Fuel consumption at idle is reported in grams/test.

APPENDIX F

TABLE F-3

FUEL CONSUMPTION (g/km)
1975 CAR, Pt (IDC) OXIDATION CATALYSTS

Kilometres		FTP	[illegible]	[illegible]	Idle[1]	64 km/h I	64 km/h	64 km/h II	96 km/h I	96 km/h	96 km/h II
0	Fuel Weight	188.8	115.8	129.1	811.7		110.4			120.3	
	Carbon Balance	181.9	112.9	125.9	1087.9	110.6		111.3	128.5		117.5
3 200	Fuel Weight	165.4	113.4	126.0	926.2		109.2			120.8	
	Carbon Balance	167.5	117.4	130.4	1019.6	110.0		105.8	117.6		115.7
6 400	Fuel Weight	164.2	108.7	123.1	826.3		108.7			113.9	
	Carbon Balance	173.7	108.2	124.2	1007.9	109.0		108.7	123.7		126.5
9 600	Fuel Weight	175.4	111.2	122.9	838.8		108.2			124.5	
	Carbon Balance	166.3	106.6	123.8	967.0	110.4		109.2	124.8		107.5
12 800	Fuel Weight	170.8	113.6	125.4	848.0		110.0			108.5	
	Carbon Balance	171.1	107.7	125.6	925.2	78.9		110.0	107.8		111.1

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(1) Fuel consumption at idle is reported in grams/test.

APPENDIX G

TABLE G-1

MAXIMUM EXHAUST GAS TEMPERATURE AT CATALYST OUTLET
Pt-Pd ([illegible])

Kilometres	Temperature, °C					
	FTP	FET	SET	Idle	64 km/h	96 km/h
0	632	554	607	382	552	571
3 200	610	582	613	391	554	607
6 400	634	554	571	346	542	593
9 600	596	560	577	374	532	577
12 800	602	582	604	377	532	577

APPENDIX C

TABLE C-2

MAXIMUM EXHAUST GAS TEMPERATURE AT CATALYST OUTLET
Pt-Rh (ABN 2/3C/408)

Kilometres	Temperature, °C					
	FTP	FET	SET	Idle	64 km/h	96 km/h
0	682	638	671	293	582	660
3 200	649	593	671	377	582	660
6 400	638	621	671	382	582	654
9 600	627	626	626	371	[illegible]78	649
12 800	649	621	660	360	571	660

APPENDIX G

TABLE G-3

MAXIMUM EXHAUST GAS TEMPERATURE AT CATALYST OUTLET
Pt (ABM 2/12C/40M)

Kilometres	Temperature, °C					
	FTP	FET	SET	Idle	64 km/h	96 km/h
0	646	627	654	343	582	652
3 200	625	630	582	388	571	593
6 400	602	571	616	371	554	593
9 600	593	577	577	377	537	577
12 800	604	582	616	396	551	627

APPENDIX H

TABLE H-1

1975 VEHICLE (351 CID)
Pt/Pd OXIDATION CATALYST* (AEW 2/8C/3D/H)

	1975 FTP, g/km					% Fuel Sulfur As	
Kilometres	**CO**	**HC**	**NO_x**	**SO_2**[a]	**$SO_4^=$**[b]	**SO_2**	**$SO_4^=$**
0	2.01	0.11	1.70	0.110	0.012	98.2	7.1
3 200	8.45(c)	0.44	1.50	0.098	0.003	89.0	1.6
6 400	9.08(c)	0.37	1.60	0.110	0.004	100.0	2.4
9 600	11.01(c)	0.73	1.78	0.093	0.004	81.6	2.3
12 800	5.87(c)	1.45	1.02	0.084	0.006	77.8	3.4

	FET, g/km					% Fuel Sulfur As	
Kilometres	**CO**	**HC**	**NO_x**	**SO_2**[a]	**$SO_4^=$**[b]	**SO_2**	**$SO_4^=$**
0	0.93	0.07	2.82	0.133	0.013	180.0	11.6
3 200	1.71	0.12	2.29	0.071	0.006	98.6	5.2
6 400	2.32	0.15	2.30	0.079	0.004	109.7	3.7
9 600	3.93	0.19	1.86	0.071	0.005	117.7	5.4
12 800	1.81	0.11	2.06	0.057	0.007	79.2	6.5

	SET, g/km					% Fuel Sulfur As	
Kilometres	**CO**	**HC**	**NO_x**	**SO_2**[a]	**$SO_4^=$**[b]	**SO_2**	**$SO_4^=$**
0	2.62	0.095	1.91	0.119	0.007	161.6	5.6
3 200	3.10	0.14	2.81	0.091	0.005	116.7	3.2
6 400	2.91	0.18	2.23	0.088	0.003	110.0	2.5
9 600	3.74	0.17	1.96	0.091	0.004	126.5	3.7
12 800	1.91	0.21	1.81	0.068	0.007	59.5	5.9

(a) SO_2 = bubbler method
(b) $SO_4^=$ = particulate-filter
(c) 2 stalls on cold start

* Visual inspection of catalysts at 12 800 km showed that one converter had been burned up.

APPENDIX H

TABLE H-2

1975 VEHICLE (351 CID)
Pt/Pd OXIDATION CATALYST* (AMW 2/6C/30/M)

	Idle, g/test					% Fuel Sulfur As	
Kilometres	CO	HC	NO$_x$	SO$_2$$^{(a)}$	SO$_4$$^{=(b)}$	SO$_2$	SO$_4^=$
0	0.17	0.60	0.80	0.666	0.046	155.6	7.2
3 200	5.79	1.97	2.61	0.491	0.010	73.5	1.0
6 400	7.60	2.71	3.02	0.502	0.012	74.7	1.1
9 600	25.82	4.75	0.66	0.260	0.032	73.0	5.9
12 800	42.29	9.96	0.04	0.179	0.022	52.0	4.2

		64 km/h, g/km					% Fuel Sulfur As	
Kilometres		CO	HC	NO$_x$	SO$_2$$^{(a)}$	SO$_4$$^{=(b)}$	SO$_2$	SO$_4^=$
0	I	0.75	0.02	0.46	0.034(c)	0.013(d)	48.6	12.4
	II	0.06	0.01	0.66		0.014		11.9
3 200	I	0.80	0.04	0.69	0.067	0.006	98.5	3.9
	II	0.79	0.04	0.68		0.010		9.8
6 400	I	1.43	0.06	0.74	0.080	0.003	117.6	2.9
	II	1.42	0.05	0.72		0.005		4.9
9 600	I	2.64	0.07	0.84	0.067	0.005	104.7	5.2
	II	3.74	0.07	0.79		0.005		5.2
12 800	I	1.44	0.06	0.86	0.059	0.005	84.3	4.8
	II	1.60	0.03	0.38		0.007		6.0

		96 km/h, g/km					% Fuel Sulfur As	
Kilometres		CO	HC	NO$_x$	SO$_2$$^{(a)}$	SO$_4$$^{=(b)}$	SO$_2$	SO$_4^=$
0	I	0.08	0.05	2.81	0.056(c)	0.040(d)	80.0	38.3
	II	0.08	0.01	2.76		0.037		35.0
3 200	I	1.11	0.05	5.17	0.084	0.018	110.5	15.8
	II	1.02	0.04	5.11		0.013		12.0
6 400	I	2.17	0.08	4.18	0.092	0.008	131.4	7.6
	II	2.27	0.07	4.61		0.007		6.7
9 600	I	3.65	0.05	2.89	0.068	0.010	113.3	10.5
	II	4.08	0.05	3.13		0.007		7.6
12 800	I	1.76	0.14	2.20	0.053	0.008	85.5	8.9
	II	1.87	0.11	2.31		0.007		7.3

(a) SO$_2$ = bubbler method
(b) SO$_4^=$ = particulate-filter
(c) One sample taken over 1 hour test
(d) One sample taken for 20 minutes during each half hour segment

* Visual inspection of catalysts at 12 800 km showed one converter had been burned up.

APPENDIX B

TABLE B-3

FUEL CONSUMPTION, (g/km)
1975 CAL. Pt-Pd (A-C) OXIDATION CATALYSTS(1)

Kilometres		FTP	HFET	SET	Idle(2)	64 km/h		96 km/h	
						I	II	I	II
0	Fuel Weight	177.2	122.9	141.6	599.3	126.0		128.3	
	Carbon Balance	176.2	126.4	131.8	667.4	129.8	120.2	108.2	111.8
3 200	Fuel Weight	181.3	123.2	137.0	335.2	122.7		128.56	
	Carbon Balance	171.6	112.8	123.8	1094.2	104.9	104.1	119.5	115.9
6 400	Fuel Weight	179.0	119.6	133.5	908.0	115.4		120.2	
	Carbon Balance	171.9	111.7	126.5	1048.7	106.4	105.6	111.0	109.0
9 600	Fuel Weight	189.0	113.1	130.4	553.9	119.0		119.1	
	Carbon Balance	188.0	101.9	121.5	594.7	106.0	109.0	99.7	105.2
12 800	Fuel Weight	181.3	116.4	128.1	558.4	116.5		122.8	
	Carbon Balance	178.3	119.1	128.1	572.0	118.5	121.4	102.3	107.9

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(1) Visual inspection of oxidation catalysts at 12 800 km showed that one converter had been burned up.

(2) Fuel consumption at idle is reported in grams/test.

APPENDIX B

TABLE B-4

MAXIMUM EXHAUST GAS TEMPERATURE AT CATALYST OUTLET
Pt-Pd ([illegible])*

	Temperature, °C					
Kilometres	FTP	FET	SET	Idle	64 km/h	96 km/h
0	638	624	660	449	571	632
3 200	582	571	571	316	510	604
6 400	549	571	571	327	516	582
9 600	560	571	582	232	549	604
12 800	549	527	549	216	527	560

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*Visual inspection of catalysts at 12 800 km showed that one converter had been burned up.